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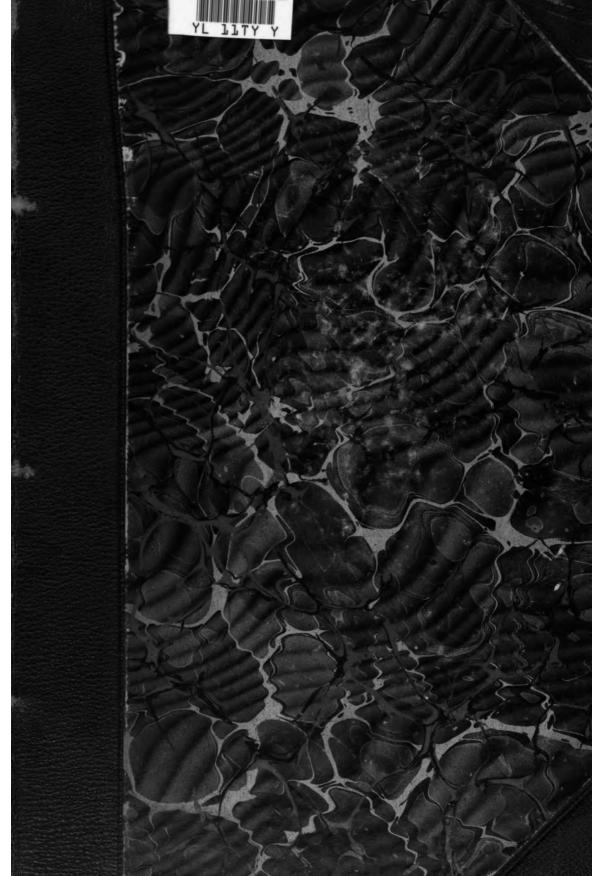
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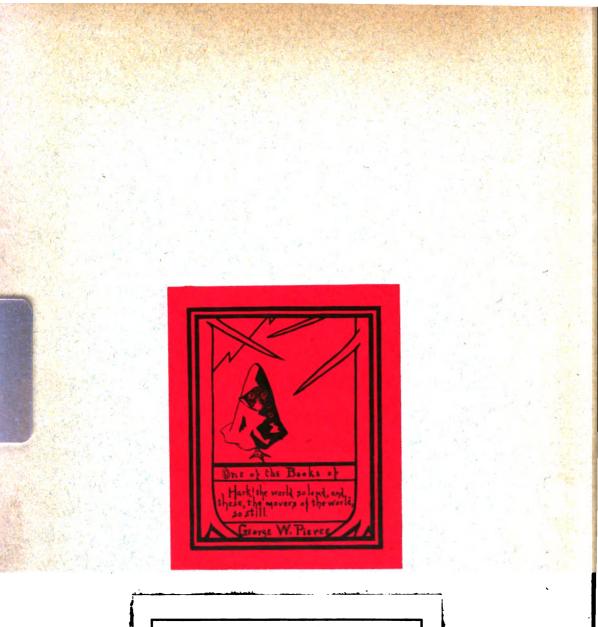
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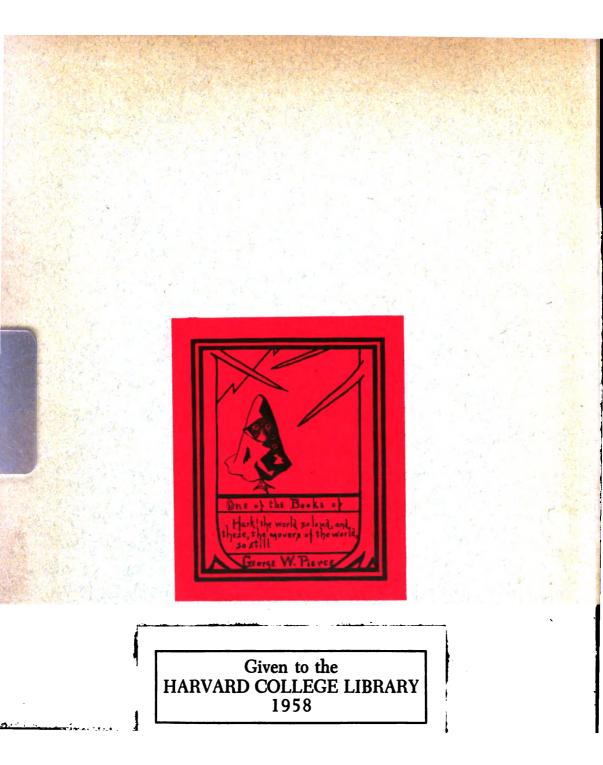




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### THE

# PHYSICAL REVIEW

A JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS

CONDUCTED WITH THE CO-OPERATION

OF THE

## AMERICAN PHYSICAL SOCIETY

BY

EDWARD L. NICHOLS, ERNEST MERRITT, AND FREDERICK BEDELL

Vol. XVII

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#### ТНЕ

# PHYSICAL REVIEW.

#### ULTRA-VIOLET ROTARY DISPERSION.

#### BY P. G. NUTTING.

THE power of rotating the plane of polarization of transmitted radiation is particularly interesting in the region of the very short wave-lengths. In the first place it affords an indication of what the limiting value of the rotation would be for infinitely short waves. From theoretical considerations we might expect this limiting value to be either zero or infinity, possibly a finite constant. Again, rotary dispersion in the ultra-violet affords valuable data for the theory of rotation in the neighborhood of an absorption band. Theoretically, we should have a greatly enhanced rotation near every absorption band and a large rotation of opposite sense in the middle of the band. Now all transmission spectra end sooner or later in the ultra-violet in an absorption band, so that the ultraviolet region is an excellent one for obtaining the data desired.

Previous work in the ultra-violet has been confined to quartz and sodium chlorate. Soret and Sarasin<sup>1</sup> have observed the rotation of quartz out as far as the cadmium line 26, wave-length 214.3  $\mu\mu$ , where they found the rotation per millimeter thickness 236 degrees, while in the yellow it is only about 21 degrees and in the infra-red small, increasing from three degrees in the yellow to fifteen degrees at 250.

Rotation in the neighborhood of an absorption band has been observed by Schmauss<sup>1</sup> working with the magnetic rotation of cyanine and other dyestuffs in alcohol solution, and by Cotton<sup>2</sup> who observed the structural rotation of copper and chromium tartrates. Zeeman<sup>3</sup> has observed the magnetic rotation of sodium vapor up to and within the lines. Several other observers have worked on anomalous rotation, that is, rotation which decreases with decreasing wave-length.

The methods available for work in the ultra-violet and in regions of strong absorption are but limited in number. Previous work has been done by visual methods with a fluorescent eyepiece. Guye used a quartz-wedge polariscope with his eyepiece. But visual methods fail when the transmitted radiation is excessively feeble and one must resort to the cumulative methods of photography. Glan or Foucault nicols can be used out as far as 230  $\mu\mu$ , where the calcite begins to absorb. Schmauss inserted a block of quartz and a plate of gypsum with his rotating column of fluid. This method might be used photographically but gypsum is opaque in the ultraviolet and suitable transparent biaxial crystals are not available. A much simpler and entirely satisfactory method was suggested by the apparatus used by Minor<sup>4</sup> for determining the refractive and absorptive indices of the metals in the ultra-violet. This method consists in inserting with the rotating column a pair of quartz rotation wedges. Such wedges produce interference bands which are easily photographed. Inserting a rotating body with the wedges produces a displacement of these bands and the amount of the shift is an accurate measure of the amount of rotation introduced.

#### Apparatus and Method.

It is, of course, a great saving of time in exposing and measuring to be able to photograph the rotation of the whole spectrum on a

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accomplish this we must get the interference bands and spectrum lines in focus at the same place, that is the rotating wedges must be placed at the slit or an image of the slit of the spectroscope used in producing the spectrum. The final arrangement adopted is shown in the figure.

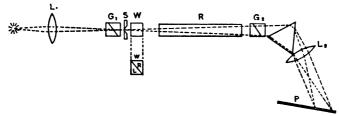


Fig. 1. Diagram of Apparatus.

An image of the spark source is thrown on the slit S and a spectrum formed on the photographic plate P. Before entering the slit, the light is polarized by the Glan nicol  $G_1$  and immediately afterward passes through the rotation wedges W. A second Glan nicol  $G_2$  is placed near the prism and the tube of rotating solution inserted between this nicol and the wedge pair. The distance  $L_1 - S$  and S - P are made very great so that the light is very nearly parallel as it passes through the wedges and rotating substance. The nicols were used parallel so that the central straight band was dark on the photographic plate.

A spark between ectrodes made of an alloy of zinc and aluminium was used as a source of radiation through all the work. The spark spectrum of this alloy contains a convenient number of lines very evenly distributed. A crystal of some sodium salt was held in the spark from time to time. This not only brought up the photographic intensity in the yellow but so increased the possible length of the spark that much more capacity could be used and the intensity of the source increased many times. The Glan nicols were 20 mm. cubes and were found to be admirably adapted to this use. The nicols do not require very accurate adjustment for this kind of

#### P. G. NUTTING.

lowered until its image very nearly bisected the central dark interference band on the photographic plate. It is then opposite that part of the wedges where they are of equal thickness. The wedges were cut to order, one of right and one of left rotating quartz 16 mm. thick and 20 mm. square. The tube R for holding the rotating liquid was closed at the ends with a pair of very carefully matched quartz plates, right and left rotating, giving no appreciable resultant rotation. These plates were 25 mm. in diameter and 2.872 mm. thick. A number of different tubes were used, some 5 cm. and some 60 cm. in length, according to the capacity and rotating power of the liquid being investigated. The tube most in use was one of glass 37 cm. in length with the ends very carefully ground to parallelism and the quartz end plates cemented on. The tube and wedge pair require very careful adjustment, otherwise the interference bands would not be regular and sharply defined. These adjustments were made by means of the reflected image of the slit, using an acetylene source. All the quartz parts of the apparatus as well as the Glan nicols, were specially ordered from Messrs. Steeg and Reuter and were of most admirable workmanship. The most difficult and important adjustment of all is finding the proper position and angle for the photographic plate in order that the image of the cross wire and the interference bands may be sharp and straight throughout the whole spectrum. The proper angle having been determined, the plate holder was provided with permanent ways and a micrometer screw. The prism was set at minimum deviation for the end of the visible spectrum, wave-length 400  $\mu\mu$ . Zero plates were taken with the tube filled with water or alcohol, with the tube empty and with the tube entirely removed. After the rotating substance had been inserted, a second photograph was taken. This showed the interference bands displaced up or down along the spectrum lines and the amount and direction of this displacement shows the amount and direction of the rotation at each wave-length. The displacements were measured with a Gaertner micrometer microscope refitted with a low power microscope TI

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matic plates were found to be entirely satisfactory. Metol-hydrochinone developer gives a hard, clear negative excellent for measuring. Over-exposure and over-development made the bands still sharper and narrower. The time of exposure varied from two minutes to half an hour.

#### OBSERVED DATA ON ROTARY DISPERSION.

Out of the large number of rotating substances available, some thirty were tried as promising transparency in the ultra-violet and of these, eight were found to be suitable for observation. The results are given in the order in which they were obtained. Of the other promising substances tried, quinine (sulphate) in water solution was found to become densely opaque just beyond the visible violet. The absorbed ultra-violet quickly precipitated the salt from a saturated solution. Morphine sulphate showed similar properties. Santonin, which possesses the extraordinary rotation of 200 degrees in the yellow and 535 degrees at the end of the visible violet,<sup>1</sup> becomes strongly absorbent just beyond. The various iron double tartrates, which absorb nearly the entire spectrum, show but moderate rotating power in their transmission bands.

Cane Sugar,  $C_{12}H_{22}O_{11}$ .—This, in concentrated solution, begins to absorb just beyond the visible, but by taking a very dilute solution and making a long exposure, the rotation was obtained out as far as wave-length 252  $\mu\mu$ . The concentration used was 3.45 grams of sugar to 100 grams of solution, density 1.013, tube length 77.32 cm., temperature 18 degrees. In the table of data below, the column marked  $\lambda$  refers to wave-lengths, that marked

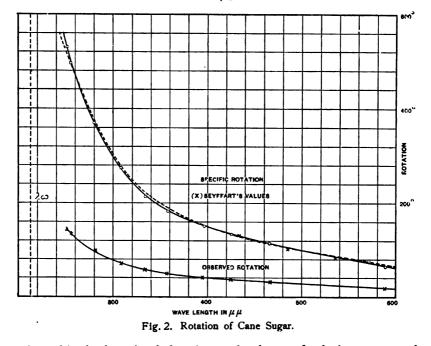
<b>x</b>	180° mm.	Ref. mm.	Ret. deg.	Null,	Ob. Rotn.	Sp. Rotn
589	3.402	1.920	101.6	83.6	18.0	66.8
467	2.134	1.311	110.7	79.6	31.1	115.2
425	1.730	1.094	113.8	77.2	36.6	134.1
395	1.492	0.954	115.0	75.4	40.6	150.4
358	1.182	0.799	121.7	72.6	49.1	182.0
334	0.992	0.708	128.7	70.8	57.9	214.8
309	0.810	0.642	142.6	68.5	74.1	274.8
281	0.637	0.588	165.1	65.6	<b>9</b> 9.5	368.9
256	0.527	0.574	196.4	62.6	133.8	496.0
252	0.486	0.554	205.7	61.9	143.8	533.5

<sup>1</sup> Nasini, Ac. dei Lincei, 3, 13, 1882.

#### P. G. NUTTING.

180° gives the width of an interference band in mm. That marked Ref. (mm). gives the distance from the image of the cross wire to the center of the interference band use for reference. Under Ref. (deg.) is given the same distance expressed in degrees. "Null" is the corresponding distance before rotation occurred. Then follow observed rotation and specific rotation.

From wave-length 358 on, the second band was used for reference instead of the first. The distances given in the third column were obtained by subtracting the width of a band from the observed distances. The specific rotation is calculated from the observed rotation by means of the formula



R = r/lpd,

where l is the length of the observed column of solution expressed in decimeters, d is the density of the solution and p is the ratio of

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#### No. 1.] ULTRA-VIOLET ROTARY DISPERSION.

The dispersion curve is remarkably uniform and shows steadily increasing values toward the shorter wave-lengths, rising well out in the absorption band at 250 to a rotation of 560°. No exterior limit to the absorption band could be observed; it probably continues through the remainder of the spectrum. Some previous observations of Seyffart in the visible spectrum are given.

Camphor,  $C_{10}H_{16}$ .— Camphor has a strong absorption beginning just beyond the visible. Readings were obtained as far as 334. The material used appeared very pure, but as camphor is such an

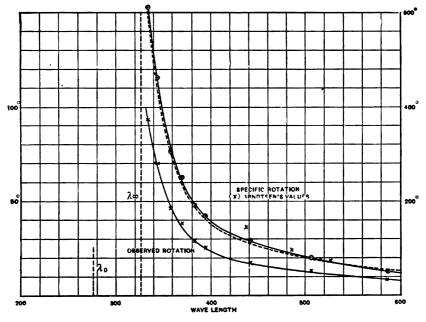


Fig. 3. Rotation of Camphor.

excellent solvent for organic impurities, it was twice distilled before dissolving in freshly distilled ethyl alcohol for use. The concentration used was 34.70 grams of camphor to 100 grams of solutional density 0.864, temperature 18°.

The curve is an excellent example of the dispersion in the neighborhood of a broad band. The dispersion remains regular and normal up to near where the absorption begins and there increases very sharply. The essentially different value obtained by Arndtsen

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#### P. G. NUTTING.

at wave-length 438 might easily have been caused by a slight shifting of the absorption band due to a trace of impurity or isomeric camphor. Camphoric acid was tried but it transmitted only the visible spectrum and its rotation showed no unusual features.

λ	180° mm.	Ref. mm.	Ref. deg.	Null.	Ob. Rotn.	Sp. Rotn
589	2.505	1.277	91.62	83.61	8.01	52.4
506	1.880	0.985	94.4	81.1	13.3	87.2
441	1.425	0.760	96.0	78.1	17.9	117.2
395	1.095	0.615	101.1	75.4	25.7	168.1
383	1.030	0.594	103.9	74.6	29.3	191.9
370	0.940	0.515	111.9	73.5	38.4	251.4
358	0.897	0.593	118.9	72.6	46.3	303.0
344	0.786	0.620	142.0	71.6	70.4	462.0
334	0.706	0.644	164.3	70.8 ·	93.5	612.5

Limonene and Pinene.— Two of the principal components of turpentine, dextro-limonene and lævo-pinene, were tested and found to absorb slightly at wave-length 420 and quite completely even in columns but 4 cm. thick at 390. The observed rotations are here recorded, however, on account of the striking dissimilarity in the

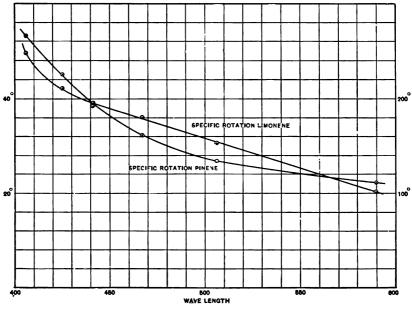


Fig. 4. Rotation of Limonene and Pinene.

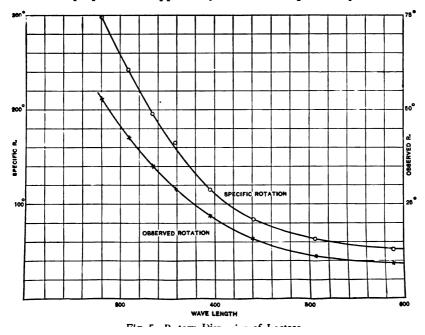
curves from the normal form that we should expect.

dispersion curves of the two substances and the departure of both

Specific Rotation.					
λ	Limonene.	Pinene.			
589	100.7	22.35			
506	153.6	26.92			
467	180.1	32.20			
441	194.5	37.64			
425	211.4	45.01			
406	248.0	53.35			

Neither curve is of the normal type as are those of sugar and camphor. The curvature of the pinene curve is remarkably uniform while that of the limonene is very small throughout most of its length.

*Lactose*, Milk Sugar,  $C_{12}H_{22}O_{11}+H_2O$ .—The lactose used was the chemical preparation supplied by Merck and proved quite trans-



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<b>X</b>	180° mm.	Ref. mm.	Ref. deg.	Null.	Ob. Rotn.	Sp. Rotn
589	2.987	1.398	84.15	95.4	9.25	52.4
506	2.250	1.047	83.83	95.0	11.17	63.3
441	1.695	0.744	77.0	94.9	15.9	90.1
395	1.219	0.444	73.1	94.9	21.8	114.2
358	1.020	0.377	66.6	95.8	29.2	165.3
334	0.855	0.294	61.9	96.9	35.0	196.4
309	0.707	0.224	57.6	100.4	42.8	242.4
281	0.581	0.171	55.2	108.1	52.9	299.5

used having the density 1.025 and containing 15.81 per cent. of lactose. The temperature was 19°.

The rotary dispersion is small and uniform, such as would correspond with a broad absorption band with diffuse edges. The curves are normal and typical.

*Maltose* and *Glucose*,  $C_6H_{12}O_6$ .— The purest chemically prepared glucose obtainable was slightly yellow in solution, absorption began

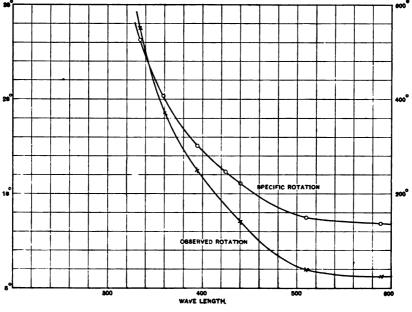


Fig. 6. Rotary Dispersion of Maltose.

in the green and became very strong in the violet. Shaking up the solution with bone-black and filtering through sand and charcoal

did not improve its transparency. Maltose proved more transparent and with a very dilute solution readings were obtained out to  $334 \mu\mu$ , The density of the solution was 1.005 and it contained 1.794 per cent. of maltose. Tube length 37.59 cm., temperature 19°.

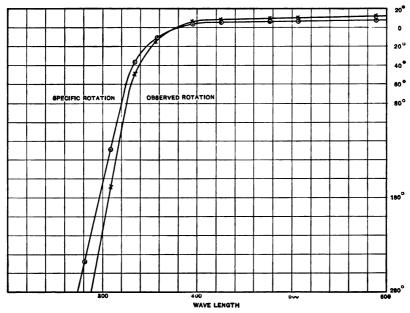
λ	180° mm.	Ref. mm.	Ref. deg.	Null.	Ob. Rota.	Sp. Rotn
589	2.918	1.394	86.10	95.41	9.31	137.5
506	2.200	1.038	84.9	95.0	10.1	149.3
441	1.684	0.750	79.9	94.9	15.0	221.9
425	1.526	0.662	78.2	94.9	16.7	246.8
395	1.290	0.537	74.4	94.9	20.5	303.0
358	1.023	0.389	68.4	95.8	27.4	405.1
334	0.85	0.29	61.4	96.9	35.5	524.8

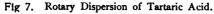
The dispersion curves are of the ordinary type except that there is a slight irregularity in the green and just beyond the visible such as would be caused by a shoulder in the absorption curve in the blue.

Tartaric Acid, H<sub>2</sub>C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>.— This, as well as nearly all of its salts, is quite transparent in the ultra-violet when very pure. Measurements were made out as far as wave-length 281 without difficulty. A water solution was used having a density 1.236 and containing 28.625 per cent. of the acid crystals.

<b>λ</b>	180° mm.	Ref. mm.	Ref. deg.	Null.	Ob. Rotn.	Sp. Rotn
589	2.982	1.362	82.35	95.4	13.05	9.82
506	2.283	1.068	84.3	95.0	10.7	8.06
467	1.894	0.895	85.0	94.9	9.9	7.49
425	1.555	0.747	86.4	94.9	8.5	6.39
395 <sup>°</sup>	1.357	0.661	87.7	94.9	+ 7.2	+ 5.42
358	1.055	0.644	109.8	95.8	-14.0	-10.58
334	0.864	0.694	144.6	96.9	47.7	35.82
309	0.721	0.829	269.0	100.4	168.6	126.8
281	0.629	1.522	436.7	108.1	328.6	247.4

The rotary dispersion of tartaric acid is remarkable for the reversal of the sense of the rotation and for the abrupt change from a small constant positive rotation in the visible spectrum to a very large negative rotation in the ultra-violet. The reversal of the limits, the sense of the rotation reverses at a certain concentration. To account for these exceptional properties of tartaric acid it is usual to assume that the molecules are not all alike in structure. But for the physical discussion of the rotary dispersion we must regard a solution of this substance as of fixed definite composition which is of course independent of the wave-length.





Ammonium Tartrate  $(NH_4)_2C_4H_4O_6$ . — A 16.24 per cent. water solution was used. Density, 1.070; temperature, 19°; tube length, 37.59 cm.

λ	180° mm.	Ref. mm.	Ref. deg.	Null.	Ob. Rotn.	Sp. Rotn
589	3.123	1.269	73.2	95.4	22.2	34.2
506	2.351	0.858	65.7	95.0	29.3	44.9
467	1.977	0.649	59.1	94.9	35.8	54.9
425	1.609	0.459	51.4	94.9	43.5	66.7
395	1.356	0.328	43.6	94.9	51.3	78.6
358	1.067	0.201	34.0	95.8	61.8	94.7
334	0.921	0.142	28.8	96.9	68.1	104.3
309	0.749	0.102	24.5	101.2	76.7	117.4
281	0.578	0.061	18.4	105.5	86.6	132.7

#### No. I.] ULTRA-VIOLET ROTARY DISPERSION.

The dispersion curves for ammonium tartrate are quite regular and are rather an extreme type of very small rate of change of dispersion like the turpentine components. Camphor and tartaric acid are the opposite extreme.

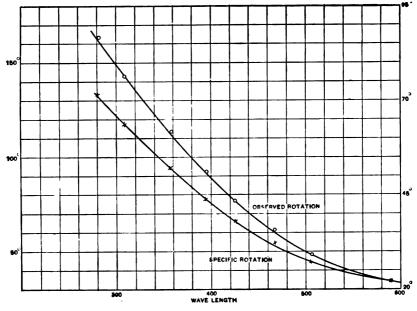


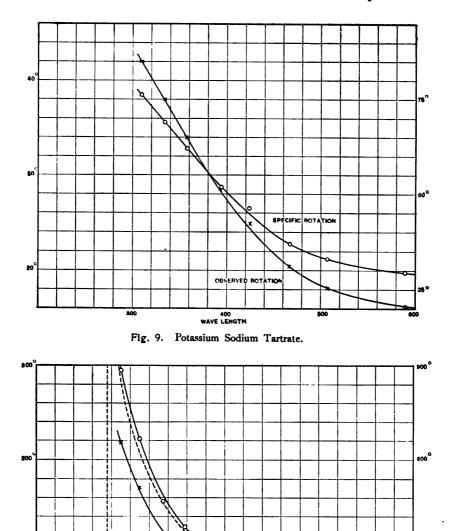
Fig. 8. Dispersion of Ammonium Tartrate.

Potassium Sodium Tartrate, Rochelle Salt,  $KNaC_4H_4O_6 + 4H_2O$ . — Water solution, density, 1.078, containing 18.75 grams of salt to 100 grams of solution. Absorption band intense beyond 300  $\mu\mu$ and extends down into the visible blue.

λ	180° mm.	Ref. mm.	Ref. deg.	Null.	Ob. Rotn.	Sp. Rotn
589	3.007	1.320	79.0	95.4	16.4	29.7
506	2.243	0.956	76.8	95.0	18.2	33.0
467	1.898	0.744	70.5	94.9	20.4	36.9
425	1.553	0.593	68.7	94.9	25.6	46.4
<b>395</b>	1.345	0.494	66.1	94.9	28.8	32.2
358	1.065	0.366	61.8	95.8	34.0	62.3
334	0.851	0.274	58.8	96.9	38.1	69.0
309	0.68	0.22	58.4	100.4	42.0	76.1

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SPECIFIC ROTATION

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#### No. 1.] ULTRA-VIOLET ROTARY DISPERSION.

The dispersion curves are of the regular form, the dispersion being unusually constant in the ultra-violet, indicating perhaps that the maximum of the absorption is still far distant or else that the absorption does not become very intense.

Potassium Antimony Tartrate, Tartar Emetic,  $2K(SbO)C_4H_4O_6 + H_2O_6$ . — Water solution, density 1.032, containing 6.635 per cent. of salt. Absorption perceptible only in the ultra-violet.

λ	180° mm.	Ref. mm.	Ref. deg.	Nuli.	Ob. Rotn	Sp. Rotn
589	2.977	1.044	63.3	95.4	32.1	124.8
506	2.247	0.681	54.6	95.0	40.4	157.0
467	1.867	0.480	46.4	94.9	48.5	188.4
425	1.527	0.283	33.4	94.9	61.5	238.8
<b>396</b> (	1.306	0.146	29.14	94.9	74.7	290.0
358 ,	1.039	1.013	175.7	95.8	100.1	388.8
334	0.868	0.751	155.7	96.9	121.2	471.0
309	0.722	0.441	110.4	101.2	170.8	663.5
290	0.644	0.24	167.3	105.5	228.2	886.5

The specific rotatory power is large even in the visible, but in the edge of the absorption band reaches the remarkable value of nine hundred degrees. The rate of increase of dispersion is remarkably uniform, like that of pinene and in marked contrast to that of camphor and tartaric acid.

These ten dispersion curves show very clearly that they could not be made congruent by merely altering the scale on which they are plotted, nor could they be made even approximately straight lines by plotting logarithms of wave-lengths instead of wave-lengths. The cane sugar, lactose and ammonium tartrate curves have somewhat the form of the exponential, but camphor, limonene, maltose and potassium antimony tartrate curves could not be represented by an exponential or logarithmic function even approximately. All the curves are of the form of parts of hyperbolas of higher degree

 $R f(\lambda) = \text{const. or } R f(\lambda) = \varphi(\lambda).$ 

But if we are to use an algebraic dispersion formula, we see from the irregularities of the curves that it must contain at least four constants. For instance, consider the simplest possible form, the Laurent expansion of the actual function whatever that is, namely:

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$$R = A + B/\lambda + C/\lambda^2 + \cdots$$

A curve like Fig. 10 could be very approximately represented by the first three terms of this series since its curvature is quite uniform. Dispersion like that of cane sugar (Fig. 2) could be represented fairly well by four terms of the series since its change of curvature is uniform. But to represent the dispersion of camphor (Fig. 3) or of tartaric acid (Fig. 7) would require at least five terms, since the curvature is at least quadratic in  $\lambda$ . Evidently no mere expansion formula will satisfactorily represent such dispersion as we have here to deal with. For use in determining the constants of dispersion formulas the following values of the rotation were taken from the plotted curves :

λ	Sugar.	Camph.	Limon.	Pinene.	Lact.	Malt.	Tart. A cid.	Am. Tart.	KNa Tart.	KSb Tart
600	62.1	46.1	95.6	21.8	51.9	135.9	9.4	32.9	29.4	125
575	71.1	54.1	111.0	22.9	53.6	138.3	8.9	35.4	29.8	128
550	80.3	62.0	126.8	24.2	56.0	141.9	8.4	38.2	30.7	135
525	89.7	71.4	142.2	25.6	59.5	145.8	7.9	41.7	31.8	143
500	99.8	81.7	158.0	27.6	64.6	157.0	7.5	45.8	33.6	158
475	110.3	94.3	173.9	30.8	71.2	176.5	7.0	51.1	35.9	177
450	122.2	109.8	189.6	36.4	80.1	207.7	6.6	57.8	39.6	204
425	134.6	129.7	211.0	44.9	92.2	246.8	6.1	65.9	44.7	238
400	149.9	158.6	290 °	56.1	110.1	291.5	6.0	75.4	50.6	281
375	167.4	221.7	l	ļ	137.3	350.7	1.4	86.0	57.3	334
350	192.9	378.3	-		171.4	440.6	16.8	97.5	67.9	418
325	252.2	1			210.9	586	56.8	109.5	78.6	548
300	297.7				258.3		166.0	121.4	88.9	758
275	394.4		1	•	310		296.8	142		1020
250	543.0						i			

#### THE MECHANISM OF ROTATION.

In attempting to develop a consistent possible mechanism of rotation and rotary dispersion, we are led at the outset to distinguish three entirely different rotatory processes, independent of one another and superposable upon each other without interference. These three processes are concerned with the magnetic rotation exhibited by all substances, the structural rotation of some crystals and torsionally strained solids and the molecular rotation shown by certain organic fluids and solids. Naturally active fluids and crystals in a magnetic field rotate just as much on their own account as though the field were not there. And in the very rare instances in which active fluids crystallize so as to rotate structurally as well, the rotation due to each mechanism may be shown to exist independently of the other. It is significant that empty ether is not even magnetically rotating, the presence of matter is necessary to give the magnetic field an effective hold on the light waves.

Dissolve in a transparent solvent a substance having a narrow absorption band and the magnetic rotation of the solution will be greatly enchanced in the neighborhood of the absorption band. But if the solvent be itself rotationally active and the absorbing solute non-active, the rotation of the solution will not differ from that of the pure solvent. The absorbing particles must form a part of the rotating molecule itself before they can affect the rotation. In crystalline rotation it is sufficient that the added particles form an integral part of the crystalline structure.

Molecular rotation is exhibited by such crystals as can occur in twin pairs, one of these forms rotating right-handedly and the other an equal amount left-handedly. The forms of these twin pairs are images of each other, but only such images as are not superposable on each other. In this case the rotation appears to be due entirely to the manner in which the molecules are packed together, for structural rotation is always lost on fusion or solution. It may be imitated by a pile of mica plates arranged with the principal section of each plate turned  $60^\circ$ ,  $90^\circ$  or  $120^\circ$  from the last. But the mechanism of the rotation caused by the mica plate pile can hardly be the same as that of active crystals.

The molecules of active fluids exhibit the same asymmetry of structure as to active crystals. The four atoms or radicles at the extremities of the four carbon bonds are such that they are capable of forming two essentially different molecular structures. These twin pairs are non-superposable images of each other. An active fluid or solution has of course the same rotating power in every direction just as a pile of active crystals would, and probably for about the same reason. Change of state does not affect molecular or magnetic rotation; even in vapor form the specific rotation is the same.

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In each of the three kinds of rotation it has been shown that a light wave is resolved into two circularly polarized components in traversing the rotating medium. Fresnel in 1823 showed the existence of circular double refraction in quartz, von Fleischl<sup>1</sup> tested active fluids and recently Brace<sup>2</sup> has shown the same to exist in magnetically active glass. Now it may be shown mathematically that the resultant of two circularly polarized waves of equal amplitude, but different (not complex) velocities is a plane polarized wave whose plane of polarization rotates as the wave advances. Hence any substance that has the power of breaking up a linear vibration into its circular components will rotate the plane of vibration, since the one essential for having this power is that right and left circularly polarized waves are transmitted with unequal velocities. If the velocities are real, say  $V_1$  and  $V_2$ , then the rotation per unit length, expressed in radians is

$$\frac{\pi}{T} \left( \frac{\mathbf{I}}{V_2} - \frac{\mathbf{I}}{V_1} \right) \text{ or } \pi \left( \frac{\mathbf{I}}{\lambda_2} - \frac{\mathbf{I}}{\lambda_1} \right)$$

where T is wave-period and  $\lambda$  wave-length. In terms of circular refractive index the rotation is therefore

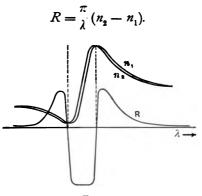


Fig. 11.

The figure shows the essential relation existing between difference in velocity (or difference in index) and rotation, independently of any theory of the mechanism of rotation. The ordinates of the

> <sup>1</sup> Wied. Ann., 24, 127, 1885. <sup>2</sup> Phil. Mag. (6), 1, 464, 1901.



rotation curve have been plotted proportional to the difference in the ordinates of the index curves. Now  $n_2$  and  $n_1$  are the same functions of  $\lambda$  and may be made congruent by changing  $\lambda$  by a constant. Call this constant  $\alpha$ . Then if  $n_1 = f(\lambda)$ ,  $n_2 = f(\lambda + \alpha)$ . On the diagram,  $\alpha$  is seen to be the distance between the maxima (or minima) of  $n_1$  and  $n_2$ . Hence  $n_2 - n_1 = f(\lambda + \alpha) - f(\lambda)$ . Expand this in a Taylor series and substitute in the above formula for the rotation and we have at once the rotatory dispersion formula

$$R = \frac{\pi}{\lambda} \left( \alpha \cdot f'(\lambda) + \frac{a^2}{2} \cdot f''(\lambda) + \cdots \right).$$

leaving the molecular (or magnetic) constant  $\alpha$  to be determined by experiment. Using but the first term of this expression, we have the familiar rotary dispersion formula

$$R = \frac{k}{\lambda} \cdot \frac{dn}{d\lambda}$$

It is remarkable that by the above formula the rotation is proportional to the tangent of the angle of slope of the index curve and the figure shows this property very clearly. If the wave velocities are complex quantities, as they are when the absorption is finite, the rotation is not so simply expressed. This case will be discussed later with the mathematical theory of rotation.

The mechanism of structural rotation is perhaps the simplest of all three kinds. That a crystal possess rotatory power it is sufficient that its dielectric elasticity be different in three different directions and that it possess the dissymmetry above mentioned. Analytically this condition of dissymmetry says that it must never be possible so to choose our coordinate system that our equations of propagation shall remain unchanged on reversal of the direction of all three coordinate axes. Such dissymmetry can be introduced by the addition of a differential quotient of uneven order to the second order term in the ordinary wave equation. Boussinesq, v. Lang, Briot, Sarrau and Drude use the differential coefficients of the first order, MacCullagh and Larmor use those of the third order. Magnetic rotation is expressed in a similar way by introducing uneven differential coefficients with regard to the time instead of a coordinate.

The mechanism of the rotation of fluids must be quite different from that of crystals. It is not sufficient to assume that the molecular elasticity, like crystalline elasticity, is different in different directions, since the light waves are so large in comparison to the molecular dimensions and the molecules of a fluid are not supposed to be so arranged that their effect would be cumulative. Nor would such intermolecular forces as the forces that would exist between the separate magnets of a freely suspended group give the molecules any selective effect on circularly polarized light waves. In any molecule except one of the very simplest type, the effect of a light wave on the charged particles of which it is composed would be to set them in motion in curved paths, but the resultant reaction of a large number of such molecules on a light wave would be zero so far as its direction of vibration was concerned. The one molecular property essential in affecting the azimuth of the wave which sets it vibrating appears to be that the charged particles of which it is composed tend to move in helical paths under the influence of a linear force. A crude analogue would be a corkscrew immersed in a fluid; a sudden impulse in the direction of its length would tend to rotate it as well as move it forward. In a medium composed of molecules having such properties, a right circularly polarized wave would travel with a different velocity from a left-handed circular wave, hence a plane polarized wave would be broken up into circular components and all the phenomena of rotation would occur. And the enantiomorphic dissymmetry above described is just what would give a molecule this rotatory property. This molecular characteristic will be the basis of the mathematical theory developed. The assumption of fixed, stable atomic orbits within the molecule is not sufficient to explain the observed phenomena of rotation as Larmor<sup>1</sup> has shown. Chiral properties depend essentially on molecular character.

#### THEORY OF ROTARY DISPERSION.

Instead of an equation stating that a linear force produces a solenoidal displacement of a charged particle, it is simpler to set up an equation which says that a solenoidal force is necessary to pro-

<sup>1</sup> Phil. Mag., 44, 503.

duce a linear displacement of the particle. Having constructed this equation of motion for a single particle, we solve it for the motion. The product of this displacement and the involved charge, summed up for all the different kinds of charged particles and summed again for all the charges of each kind in a unit volume, gives the total electric displacement. Substituting this electric displacement in the general Maxwell equations and taking the periodic solution for the motion, we have in the velocity of propagation of these waves the dispersion theory desired.

Now in general a charge e is acted on with a force eX by an electric force X. The displacement of the charge will be resisted by an inertia force, an elastic force and a frictional force. Hence

(1) 
$$eX = m \frac{\partial^2 \xi}{\partial t^2} + \frac{4\pi e^2}{\theta} \xi + \varphi e^2 \frac{\partial \xi}{\partial t},$$

where *m* is the mass to which the charge *e* is supposed to be attached and  $\hat{\boldsymbol{\varepsilon}}$  its displacement.  $\theta$  measures the ease with which the charge is displaced elastically, the factor  $e^3$  indicating that it is independent of the sign of the charge.  $\varphi e^2$  is the frictional coefficient, also independent of the sign of the charge. Now when the molecules are of the rotating kind, a solenoidal force proportional to  $\frac{\partial Y}{\partial z} - \frac{\partial Z}{\partial y}$  must be added to the linear force *eX* to produce the linear displacement  $\hat{\boldsymbol{\varepsilon}}$ . We have then <sup>1</sup> as an extension of (1) to the motion of the charged particles composing a rotating molecule :

(2) 
$$\epsilon \left[ X + \rho \left( \frac{\partial Y}{\partial z} - \frac{\partial Z}{\partial y} \right) \right] = m \frac{\partial^2 \xi}{\partial t^2} + \frac{4\pi e^2}{\theta} \xi + \varphi e^2 \frac{\partial \xi}{\partial t}.$$

If now there be N of these charged particles alike in unit volume, the current density for this kind is  $u_1 = eN d\hat{z}/dt$ . Now we are dealing with substances (non metals) in which elastic forces exist and  $\theta$  is finite. Hence motion of the charged particle will be periodic, say  $\hat{z} = Ae^{i\hat{r}}$ . Substituting in (2) and solving for  $e\hat{z}$ , the electric displacement concerned in the motion of the particle, we get for the current density :

<sup>1</sup> Drude, assuming quite a different mechanism of rotation, arrives at a similar equation. (See his Lehrbuch der Optik, p. 370.) The simple and ingenious development here presented (equations I to I3) is, I believe, due almost entirely to him.

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(3) 
$$u_{1} = \frac{\theta N}{4\pi \left(1 + i\frac{a}{\tau} - \frac{b}{\tau^{2}}\right)} \frac{\partial}{\partial t} \left[ X + \rho \left( \frac{\partial Y}{\partial z} - \frac{\partial Z}{\partial y} \right) \right]$$

where

 $a \equiv \varphi \theta / 4\pi$  and  $b \equiv m \theta / 4\pi e^2 \equiv \tau_1^2$ .

Hence the total current density arising from the displacements of all the charged particles of all kinds and of the free ether as well is:

(4) 
$$u = \frac{1}{4\pi} \frac{\partial}{\partial t} \left[ \varepsilon X + \rho \left( \frac{\partial Y}{\partial z} - \frac{\partial Z}{\partial y} \right) \right]_{t}$$

where  $\varepsilon$  is the general (average) dielectric constant of the charge imbedded ether. Hence comparing with (3),  $\varepsilon$  is seen to be

(5) 
$$\varepsilon = \mathbf{I} + \Sigma \frac{\theta_1 N_1}{\mathbf{I} + i \frac{a}{\tau} - \frac{b}{\tau^2}}$$

and

$$\rho = \Sigma \frac{\theta_1 \rho_1 N_1}{1 + i \frac{a}{\tau} - \frac{b}{\tau^2}}.$$

To get the equation for the propagation of a wave in a rotating medium, we have only to substitute the generalized current (4) in the fundamental Maxwell equations. We thus obtain three equations of the type:

(6) 
$$\frac{1}{V^2} \frac{\partial^2}{\partial t^2} \left[ \varepsilon X + \left( \rho \frac{\partial Y}{\partial z} - \frac{\partial Z}{\partial y} \right) \right] = \Delta X.$$

For a beam of light travelling along the Z axis we put

(7) 
$$X - Ae^{\frac{i}{\tau}(t-ps)}, Y = Be^{\frac{i}{\tau}(t-ps)}, Z = 0,$$

where p is the reciprocal of the velocity of propagation and A and B are complex constants. Substituting in (6), we have to determine the velocity and amplitude and of the wave propagated the two equations:

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Replacing A by A + iA' and B by B + iB', we find equations (8) to be satisfied by the two sets of values :

(9) 
$$\begin{aligned} \varepsilon - p^2 V^2 &= -p\rho/\tau, \ A = B'\\ \varepsilon - p^2 V^2 &= +p\rho/\tau, \ B = A'. \end{aligned}$$

Hence the velocity of propagation is double-valued, its reciprocal being :

(10) 
$$p = \pm \frac{\rho}{2\tau V^2} + \frac{1}{V} \sqrt{\frac{\rho^3}{4\tau^2 V^2}} + \varepsilon.$$

Call these two values  $p_1$  and  $p_2$ . Substituting in (7) and taking real parts we have the two circular waves

(11) 
$$\begin{array}{l} X_1 = A \cos 2\pi/T(t-p_1 z), \quad Y_1 = A \sin 2\pi/T(t-p_1 z), \\ X_2 = A \cos 2\pi/T(t-p_2 z), \quad Y_2 = -A \sin 2\pi/T(t-p_2 z). \end{array}$$

When the rotation factor  $\rho$  is positive, the second (clockwise) wave is the faster of the two. The resultant of the two waves is

$$X = X_{1} + X_{2} = 2A \cos \frac{1}{\tau} \left( t - \frac{p_{2}}{2} + \frac{p_{1}}{2} z \right) \cos \frac{1}{\tau} \frac{p_{2} - p_{1}}{2} z,$$
(12)
$$Y = Y_{1} + Y_{2} = 2A \cos \frac{1}{\tau} \left( t - \frac{p_{2} + p_{1}}{2} z \right) \sin \frac{1}{\tau} \frac{p_{2} - p_{1}}{2} z,$$

which is a plane polarized wave whose azimuth changes steadily with Z. At any z, the azimuth of the plane of polarization is given by

$$Y/X = \tan \frac{1}{\tau} \frac{p_2}{2} + \frac{p_1}{2} z.$$

Hence in traversing a path of length l, the plane of polarization is rotated through the angle (expressed in radians)

(13) 
$$R = \frac{l}{\tau} \frac{p_2 - p_1}{2} = \frac{l}{\tau} \cdot \frac{\rho}{2\tau V^2} = \frac{l}{\tau V} \frac{n_2 - n_1}{2}$$

where n is the refractive index for circularly polarized waves. These expressions are of the same general form as those previously arrived at from geometrical considerations, but we are now in a position to interpret the rotation constant and the circular refractive indices. The rotation constant itself,  $\rho$  is proportional to the number of charges per unit volume and hence in a manner to the optical density. It is roughly proportional to the elastic resistance to displacement and to the ratio of charge to mass (cf. equations 5 and 3). Writing (13c) in the form

$$R = \frac{l}{4^{\tau} V n} (n_2^2 - n_1^2),$$

and getting *n* from (5) by writing  $n^2(1-ix)^2 = \epsilon$ , x being the absorptive index for circularly polarized waves, we obtain for the rotation

(14) 
$$R = \frac{l\tau}{4nV} \Sigma \frac{\theta_2(\tau^2 - \tau_2^2) - \theta_1(\tau^2 - \tau_1^2)}{(\tau^2 - \tau_1^2)^2 + a\tau^2},$$

a function having the general form of that represented in Fig. 11.

Now the refractive index of the fluids investigated has not been determined and (14) is further inconvenient on account of there being so many constants to determine. A formula just as simple and not containing *n* may be obtained by substituting (5b) directly in (13b). Retaining only the real part

$$R = \frac{l}{2\lambda^2} \sum_{i=1}^{j} \frac{\theta_1 \left(1 - \frac{\tau_1^2}{\tau^2}\right)}{\left(1 - \frac{\tau_1^2}{\tau^2}\right)^2 + \frac{a_1}{\tau^2}}$$

Now the experimental work relates to a region in which  $\tau$  is much greater than  $\tau_1$ , hence neglecting the fourth power of that quantity in comparison with the second, we have finally the working formula

(15) 
$$R = \frac{k_1(\lambda^2 - \lambda_1^2)}{\lambda^2(\lambda^2 - 2\lambda_1^2 + a_1)} + \frac{k_2(\lambda_2 - \lambda_2^2)}{\lambda^2(\lambda^2 - 2\lambda_2^2 + a_2)} + \cdots$$

This formula fulfils all of the four conditions we have to impose upon it. Far from any region of absorption it expresses the inverse square law. Approaching a region of absorption, the denominator will approach the value zero more rapidly than the numerator and hence the rotation will increase much more rapidly than the inverse square of the wave-length. Within the region of absorption, for  $\lambda^2$ between  $\lambda_0^2$  and  $2\lambda_0^2 - a$ , the rotation is reversed in sign. It remains but to test the formula for the fourth requirement, namely that it closely represent the observed data using but one or two terms.



Using two terms, the observed and calculated curves would lie so near together as hardly to be distinguishable, since there would be six constants involved and the two curves would cross in at least six different places. However, using but a single term, the calculated curve lies very close to the observed. This single term test is the severest that could be applied, and the close agreement shows beyond question that the derived dispersion function is of the proper form. Since the absorption is not confined to a narrow band, we ought properly to take the sum of a number of terms having constants very nearly alike, but it may be shown mathematically that such a sum is very approximately equivalent to a single term with different constants. The constants determined for the single term formula are given below. Since differences of small quantities are involved, it is necessary to carry the calculations to seven figures.

	λο	λ <sub>e</sub>	a	k
Cane sugar.	189.6317	213.2	0.0287058	22.7886
Camphor.	276.0559	326.05	0.0461062	16.2606
Tartaric acid.	373.300	257.7	0.211035	3.5006
Potas. ant. tartrate.	254.6130	274.9	0.0540385	38.9839

The constant k gives the rotation in degrees instead of radians.  $\lambda_0$  is the wave-length at which the dispersion curve would cross the wave-length axis if produced.  $\lambda_{\infty}$ , where  $\lambda_{\infty}^2 = 2\lambda_0^2 - a$ , is the ordinate toward which the dispersion curve tends to approach asymptotically. Very roughly, the smaller  $\lambda_0$ , the straighter the curve. The larger the constant a, the greater the departure from the  $1/\lambda^2$  law.

The curves calculated with the above constants are shown dotted in the figures. The characteristic (one term) form of the dispersion curve is seen to be midway between the extreme types observed, less nearly the arc of a circle than potassium antimony tartrate and not so much the shape of a sled runner as the sugar and camphor curves.

In conclusion I desire to express my warmest thanks to Professor Nichols, of the Physics Department, and to Professor Orndorff and Mr. Teeple, of the Department of Chemistry, for their unfailing courtesy in placing at my disposal the resources of their respective departments.

CORNELL UNIVERSITY, April, 1903.

#### THE PRESSURE DUE TO RADIATION.

(SECOND PAPER.)

BY E. F. NICHOLS AND G. F. HULL.

I N a preliminary communication to the American Physical Society, meeting with Section B of the American Association for the Advancement of Science at Denver, August, 1901, the writers presented the results of observations they had made on the pressure due to radiation. An abstract of that paper appeared in Science, October, 1901, and the full paper in this journal in November of the same year. In the present paper the writers wish to present a more complete historical statement than appeared in the preliminary paper, alterations which were made in the earlier methods, and more recent observations and data under conditions permitting greater accuracy in measurement.

As early as 1619 Kepler<sup>1</sup> announced his belief that the solar repulsion of the finely divided matter of comets' tails was due to the outward pressure of light. On the corpuscular theory of light Newton<sup>2</sup> considered Kepler's idea as plausible enough, but he was of the opinion that the phenomenon was analogous to the rising of smoke in our own atmosphere. In the first half of the eighteenth century DeMairan and DuFay<sup>3</sup> contrived elaborate experiments to test this pressure of light theory in the laboratory, but, because of the disturbing action of the gases surrounding the illuminated bodies employed in the measurements, they obtained wholly confusing and contradictory results. Later in the same ceutury the Rev. A. Ben-

<sup>1</sup> De Mairan, Traité physique et historique de l'Aurore Boréale (seconde edition), pp. 357-358, Paris, 1754.

<sup>2</sup> Isaaci Newtoni, Opera quae Existent Omnia. Samuel Horsley, LL.D., R.S.S., Tom. III., pag. 156, Londinium, 1782.

<sup>3</sup> De Marian, l. c., p. 371. This treatise contains also the accounts of still earlier experiments by Hartsoeker, p. 368, and Homberg, p. 369. The later experiments are of more historic than intrinsic interest.

net<sup>1</sup> performed further experiments but could find no repulsive force not traceable to convection currents in the gas surrounding the body upon which the light was projected, due in his opinion to the heating effect of the rays. Finding no pressure due to radiation, he made the following unique suggestion in support of the wave theory of light: "Perhaps sensible heat and light may not be caused by the influx or rectilinear projection of fine particles, but by the vibrations made in the universally diffused caloric or matter of heat or fluid of light. I think modern discoveries, especially those of electricity, favor the latter hypothesis." In the meantime Euler,<sup>2</sup> accepting Kepler's theory attributing the phenomenon of comets' tails to light pressure, had hastened to the support of the wave theory by showing theoretically that a longitudinal wave motion might produce a pressure in the direction of its propagation upon a body which checked its progress. In 1825 Fresnel<sup>3</sup> made a series of experiments, but arrived at no more definite conclusion than that the repulsive and attractive forces observed were not of magnetic nor electric origin.

Crookes ' believed in 1873 that he had found the true radiation pressure in his newly invented radiometer and cautiously suggested that his experiments might have some bearing on the prevailing theory of the nature of light. Crookes' later experiments and Zöllner's <sup>5</sup> measurements of radiometric repulsions showed that the radiometric forces were in some cases 100,000 times greater than the light pressure forces with which they had been temporarily confused. Zöllner's experiments are among the most ingenious ever tried in this field of work, and he missed the discovery of the true radiation pressure by only the narrowest margin. An excellent bibliography of the whole radiometric literature is given by Graetz,<sup>6</sup> and an account of some of the older experiments not mentioned above is given by Crookes.<sup>7</sup>

- <sup>1</sup>A. Bennet, Phil. Trans., p. 81, 1792.
- <sup>2</sup> L. Euler, Histoire de l'Academie Royale de Berlin (2), p. 121, 1746.
- <sup>8</sup>A. Fresnel, Ann. Chem. et Phys., XXIX., pp. 57, 107, 1825.
- \*W. Crookes, Phil. Trans., p. 501, 1873.
- <sup>5</sup> F. Zöllner, Pogg. Ann., CLX., pp. 156, 296, 459, 1877.
- <sup>6</sup>L. Graetz, Winkelmann's Handbuch der Physik, 2 b, p. 262. Breslau, 1896.
- <sup>7</sup> W. Crookes, l. c., p. 501.

In 1873 Maxwell,<sup>1</sup> on the basis of the electromagnetic theory, showed that if light were an electromagnetic phenomenon, pressure should result from the absorption or reflection of a beam of light. After a discussion of the equations involved, he says : "Hence in a medium in which waves are propagated there is a pressure in the direction normal to the waves and numerically equal to the energy in unit volume." Maxwell computed the pressure exerted by the sun on the illuminated surface of the earth and added : "It is probable that a much greater energy of radiation might be obtained by means of the concentrated rays from an electric lamp. Such rays falling on a thin metallic disc, delicately suspended in a vacuum, might perhaps produce an observable mechanical effect."

Apparently independent of Maxwell, Bartoli<sup>2</sup> announced in 1876 that the Second Law of Thermodynamics required the existence of a pressure due to radiation numerically equal in amount to that derived by Maxwell. Bartoli's reasoning holds for all forms of energy streams in space and is of more general application than Maxwell's equations. Bartoli contrived elaborate experiments to verify this theory, but was balked in the search, as all before him had been, by the complicated character of the gas action which he found no way of eliminating from his experiments.

After Bartoli's work the subject was dealt with theoretically by Boltzmann,<sup>3</sup> Galitzine,<sup>4</sup> Guillaume,<sup>5</sup> Heaviside,<sup>6</sup> and more recently by Goldhammer.<sup>7</sup> Fitzgerald,<sup>8</sup> Lebedew,<sup>9</sup> and Hull<sup>0</sup> have discussed the bearing of radiation pressure upon the Newtonian law of gravitation with special reference to the repulsion of comets' tails by the sun.

<sup>1</sup>J. C. Maxwell, A Treatise on Electricity and Magnetism (1st edition), II., p. 391, Oxford, 1873.

<sup>2</sup> A. Bartoli, Sopra i movementi prodotti della luce e dal calorie, Florence, Le Monnier (1876), also Nuovo Cimento, XV., p. 193, 1884.

<sup>3</sup>L. Boltzmann, Wied. Ann., XXII., pp. 31, 291, 1884.

<sup>4</sup> B. Galitzine, Wied. Ann., XLVII., p. 479, 1892.

<sup>5</sup>Ch. Ed. Guillaume, Arch. de Gen. (3), XXXI., p. 121, 1894.

60. Heaviside, Electromagnetic Theory, I., p. 334, London, 1893.

<sup>7</sup> D. A. Goldhammer, Ann. Phys., IV., p. 834, 1901.

<sup>8</sup>G. F. Fitzgerald, Proc. Roy. Soc. Dub., 1884.

<sup>9</sup> P. Lebedew, Wied. Ann., XLV., p. 292, 1892. Astrophys. Jour., XIV., p. 155, 1902.

<sup>0</sup>G. F. Hull, Trans. Astron. Soc. Toronto, p. 123, 1901.

#### No. 1.] THE PRESSURE DUE TO RADIATION.

The theory of radiation pressure combined with the known properties of negative electrons has recently been more or less speculatively applied by Arrhenius<sup>1</sup> to the explanation of many cosmical and terrestrial phenomena among which the following may be mentioned: The solar corona, zodiacal light, gegenschein, comets, origin of cometary and meteoric material in space, the emission of gaseous nebulæ, the peculiar changes observed in the nebula surrounding Nova Persei, the northern light, the variations in atmospheric electricity and terrestrial magnetism and in the barometric pressure. Swartzschild<sup>2</sup> computed from radiation pressure on small spherical conductors the size of bodies of unit density for which the ratio of radiation pressure to gravitational attraction would be a maximum.

Before the Congrès International de Physique in 1900, Professor Lebedew,<sup>3</sup> of the University of Moscow, described an arrangement of apparatus which he was using at that time for the measurement of light pressure. He summarizes the results already obtained as follows: "Les résultats des mesures que j'ai faites jusqu'ici peuvent se résumer ainsi: L'expérience montre qu'un faisceau lumineux incident exerce sur les surfaces planes absorbantes et réfléchissantes des pressions qui, aux erreurs près d'observation, sont égales aux valeurs calculées par Maxwell et Bartoli." No estimate of the "errors of observation" was given in the paper nor other numerical data. Unfortunately the proceedings of the Paris Congress did not reach the writers nor any intimation of the methods or results of Professor Lebedew's work until after the publication of their own preliminary experiments.

In the preliminary paper already referred to, the writers presented the results they had obtained by measurement of radiation pressure at various gas pressures. The main arguments underlying the method of measurement of the radiation pressure follow.

In the experiments of earlier investigators every approach to the experimental solution of the problem of radiation pressure had been

<sup>3</sup> P. Lebedew, Rapports présentés au Congrès International de Physique (2), p. 133, Paris, 1900.

<sup>&</sup>lt;sup>1</sup>S. A. Arrhenius, Lehrbuch der Cosmischen Physik, Leipzig, 1903, pp. 149-158, 200-208, 226, 920-925.

<sup>&</sup>lt;sup>2</sup>K. Swartschild, Kgl. Bayer. Akademie d'Wissenschaften, XXXI., 293, 1901.

balked by the disturbing action of gases which it is impossible to remove entirely from the space surrounding the body upon which the radiation falls. The forces of attraction or repulsion, due to the action of gas molecules, are functions, first, of the temperature difference between the body and its surroundings, caused by the absorption by the body of a portion of the rays which fall upon it; and second, of the pressure of the gas surrounding the illuminated body. In the particular form of apparatus used in the present study the latter function appears very complicated, and certain peculiarities of the gas action remain inexplicable upon the basis of any simple group of assumptions which the writers have so far been able to make.

Since we can neither do away entirely with the gas nor calculate its effect under varying conditions, the only hopeful approach which remains is to devise apparatus and methods of observation which will reduce the errors due to gas action to a minimum. The following considerations led to a method by which the elimination of the gas action was practically accomplished in the present experiments.

I. The surfaces which receive the radiation, the pressure of which is to be measured, should be as perfect reflectors as possible. This will reduce the gas action by making the rise of temperature due to absorption small, while the radiation pressure will be increased; the theory requiring that a beam, totally reflected, exert twice the pressure of an equal beam, completely absorbed.

2. By studying the action of a beam of constant intensity upon the same surface surrounded by air at different pressures, certain pressures may be found where the gas action is less than at others.

3. The apparatus — some sort of torsion balance — should carry two surfaces symmetrically placed with reference to the rotation axis, and the surfaces on the two arms should be as nearly equal as possible in every respect. The surfaces or vanes should be so constructed that if the forces due to gas action (whether suction or pressure on the warmer surface) and radiation pressure have the same sign in one case, a reversal of the suspension should reverse the gas action and bring the two forces into opposition. In this way a mean of the forces on the two faces of the suspension should be, in part at least, free from gas action.

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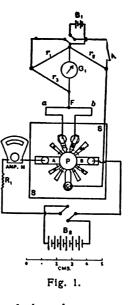
4. Radiation pressure, from its nature, must reach its maximum value instantly, while observation has shown that gas action begins at zero and increases with length of exposure, rising rapidly at first, then more slowly to its maximum effect, which, in many of the cases observed, was not reached until the exposure had lasted from two and a half to three minutes. For large gas pressures, an even longer exposure was necessary to reach stationary conditions. The gas action may be thus still further reduced by a ballistic or semiballistic method of measurement.

Ballistic observations of radiation pressure were made at air pressures ranging from 96.3 mm. to 0.06 mm. of mercury. The average radiation pressure of the standard beam was found to be

 $1.05 \times 10^{-4}$  dyne with a probable error of 6 per cent. To compare this value of the pressure with the theoretical value as given by the Maxwell-Bartoli formula,

$$p = \frac{E(1+\rho)}{V},$$

it was necessary to measure E, the energy of the beam. This was done by measuring the resistance of a platinum disc P(Fig. 1) when it was exposed to the radiation and by determining the heat generated in P by an electrical current across ABwhen the resistance of P was equal to the value it possessed when it was exposed to the beam. Using the value of the energy thus obtained and  $0.92^{1}$  as the reflection



coefficient of the silver surfaces, it was found that the pressure directly observed was about 20 per cent. lower than that computed from Maxwell's formula.

After the publication of the paper it was discovered that in dissolving the silver from the platinum when the bolometer was made, the acid had eaten away the silver from the strips A and B for a

<sup>&</sup>lt;sup>1</sup>This value was obtained from the measurements of Langley, Rubens, Nichols and Paschen for the assumed mean wave-length of the energy of the beam.

distance of nearly a millimeter under the asphalt coating. The resistance 0.278 ohm given for the disc was thus too high. It was impossible to redetermine the resistance by the direct method because of an accident to the bolometer by which the disc was nearly severed from the strip B. The disc, was therefore carefully torn away from its supports, mounted on a glass plate and cut on a dividing engine into strips, I and 2 mm. wide, parallel to AB. The resistance along these strips was measured by the fall of potential method. The resistance was found to vary slightly in different parts of the disc due to lack of uniformity in the thickness of the metal. After many measurements, an average value was reached and the resistance of the disc computed theoretically as follows:—

The resistance of a conducting sheet of infinite extent, when the current enters and leaves the sheet by electrodes<sup>1</sup> of relatively great conductivity, is  $\sigma/4\pi C$ , where  $\sigma$  is the resistance of any square of the sheet, and C is the electrostatic capacity of the two electrodes. If the electrodes are cylinders, the lines of flow are circles orthogonai to them. When the sheet, in place of being infinite, is bounded by one of these circular lines of flow, the resistance is  $\sigma/2\pi C$ . In particular if the electrodes of radii r are on a diameter of this circular sheet of radius R, then the resistance can be shown to be

$$\frac{\sigma}{\pi}\log_{\bullet}\frac{2r^2+R^2+R}{2r^2}\frac{\sqrt{4r^2+R^2}}{2r^2}.$$

Assuming for the moment that the leading-in strips of the bolometer (Fig. 1) were of great conductivity compared to that of the thin platinum sheet and that they terminated in circular arcs orthogonal to this circular sheet, the resistance would be, giving to r the value of 2.79 mm. and to R the value 11.25 mm.,  $0.922 \times \sigma$ . But the leading-in strips terminated on the boundary of the large circle. The resistance was therefore altered by two facts — the lines of flow were changed and the distance between the electrodes was increased. The latter is the important item. It is necessary therefore to find approximately the resistance of these gibbous portions of the large disc previously considered as electrodes. This may be done by estimating the area of these parts and by considering the average

<sup>1</sup> J. J. Thomson, Electricity and Magnetism, 2d edition, p. 314, Cambridge, 1897.

equipotential line as midway between the cord and arc of the cylindrical electrode. It results that the amount to be added on account of this calculation is  $0.471 \times \sigma$ . Hence the resistance between the electrodes is now  $(0.922 + 0.471) \sigma = 1.393 \times \sigma$ . The value of  $\sigma$  as found by the fall of potential method was 0.148 at  $19^{\circ}$  C. When corrected for the temperature of the disc exposed to the lamp,  $\sigma$  becomes 0.160. Hence the resistance of the disc when hot was  $1.393 \times 0.160 = 0.221$  ohm.<sup>1</sup> Substituting this computed value of the resistance in place of the one used, the energy of the standard beam becomes  $0.221 \times 0.75 \times 10^{7}$  ergs-seconds and

$$p = \frac{1.92 \times 0.221 \times 0.75 \times 10^{7}}{3 \times 10^{10}} = 1.05 \times 10^{-4} \text{ dynes.}$$

This result is in accidental agreement with the observed pressure. If necessary corrections, determined by later experiment, had been applied, the difference between the observed pressure and the pressure computed from the energy measurements would have been about three per cent. Moreover the probable error of the final result was roughly double this amount.

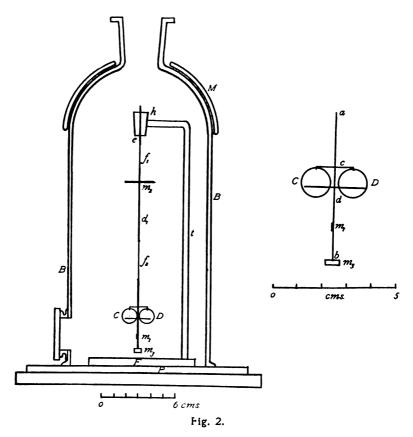
In the November number of the Annalen der Physik for 1901 Professor Lebedew<sup>3</sup> published the results of a more varied series of measurements of radiation pressure than the early measurements of the present writers. The principal difference between the methods employed by him and by the writers for determining the pressure was that he used very thin metallic vanes surrounded by gas at extremely low pressures, thus following Maxwell's suggestion literally, while the writers used silvered glass vanes and worked at large gas pressures for which the gas action had been carefully and exhaustively studied and found to be negligibly small for short exposures. From our knowledge of the variation of gas action in different vacua, we feel sure that our method would not have been successful in high vacua because of the relatively large gas action. Professor Lebedew's own results, with blackened vanes of lower heat conductivity, show that his success in eliminating gas distur-

<sup>&</sup>lt;sup>1</sup> The resistance of a trial disc was measured experimentally with the result that the experimental value differed from the theoretical by about one per cent.

<sup>&</sup>lt;sup>2</sup> P. Lebedew, Ann. Phys., VI., 433, 1901.

bance was due to the high heat conductivity of thin vanes rather than to the high vacua employed.

Professor Lebedew's<sup>1</sup> estimate of the accuracy of his work is such as to admit of possible errors of twenty per cent. in his final results. An analysis of Professor Lebedew's paper and comparison with our preliminary experiments seems to show that his accidental errors were larger than ours, but through the undiscovered false resistance in the bolometer our final results were somewhat further from the theory than his. Either of the above researches would have been sufficient to establish the *existence* of a pressure due to radiation, but neither research offered, in our judgment, a satisfactory *quantitative* confirmation of the Maxwell-Bartoli theory.



<sup>1</sup> P. Lebedew, Ann. Phys., VI., 457, 1901.



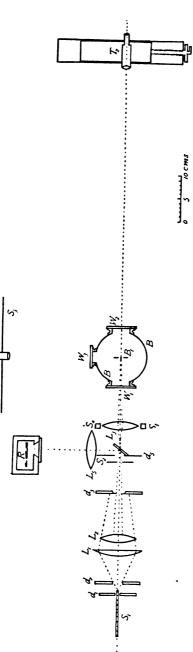
#### LATER PRESSURE MEASUREMENTS.

# Description of Apparatus.—The Torsion Balance.

The form of suspension of the torsion balance, used to measure radiation pressure in the present study, is seen in Fig. 2 and is described in detail in our preliminary paper. Its essential parts are a fine glass rod ab to which was attached a weight  $m_3$ , a scale mirror  $m_1$ , a cross arm c holding the mirrors C and D; a quartz fiber  $f_2$ ; a glass rod  $d_1$  to which was attached a small magnet  $m_2$  and a silk fiber  $f_1$ . The cover glasses C and D which served as vanes were silvered and brilliantly polished and were so hung on the small hooks that both silver or both glass faces were presented to the light. A semicircular magnet M, fitted to the vertical curvature of the bell-jar, was used to direct the suspended magnet  $m_2$  and thus to control the zero position of the torsion balance. By turning Mthrough 180°, the opposite faces of the vanes C and D could be presented to the light.

#### THE ARRANGEMENT OF APPARATUS.

A horizontal section of the apparatus through the axis of the light beam is shown in Fig. 3. An image of the aperture  $d_{s}$ , very brightly illuminated by the white-hot carbon  $S_1$  and the lenses  $L_1$ and  $L_2$ , was formed by the lens  $L_3$  in the plane  $B_1$ . A shutter  $S_2$ controlled by a magnetic escapement operated by the seconds contact of a standard clock permitted the exposure of the beam upon the vanes for any whole number of seconds. The stops  $S_s$  and  $S_s$ were so arranged that when the lens  $L_s$  was against either stop the image of  $d_s$  was central upon one of the vanes. A glass plate inclined at an angle of  $45^{\circ}$  to the axis of the beam and a lens  $L_s$ gave an image of  $d_3$  upon one arm of the bolometer at R. This bolometer was of sheet platinum 0.001 mm. thick rolled in silver. The strip was cut out in the form shown in Fig. 4, and mounted on a thin sheet of slate S. Two windows had been cut in the slate behind the strips at AB, CD where the silver had been removed, leaving the thin platinum. The platinum surfaces were blackened by Kurlbaum's process. The image from  $L_s$  (Fig. 3) fell at D. The silver ends between A and C were connected with E and F respec-



various parts about the axis of rotation.

tively. On the heavy wire EF a sliding contact c served to balance the bridge, all four arms of which are shown in the figure.

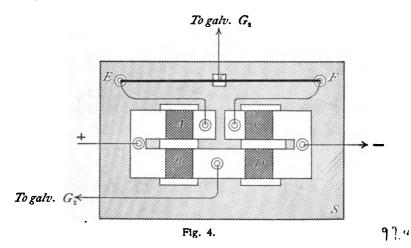
METHODS OF OBSER-VATION.

The observations leading to the results given later were of three different kinds: (1) The calibration of the torsion balance; (2) the measurement of the pressure of radiation of the law in Flg. J. terms of the constant of the balance; and (3) the measurement of the energy of the same beam in erg-seconds by the rate of temperature rise of a blackened silver disc, of known mass and specific heat.

> I. The determination of the constant of the torsion balance was made by removing the vanes Cand D and accurately measuring the period of vibration. Its moment of inertia was easily computed from the masses and distribution of the The moment of torsion

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for 1 mm. deflection on a scale 105 cm. distant was  $0.363 \times 10^{-5}$  dyne  $\times$  cm. This value divided by one half the distance between the centers of the light spots on the two vanes gave the force in dynes per scale division deflection. As the light spots were circles



11.25 mm. in diameter the area of the image was very nearly 1  $(cm.)^2$ , hence the above procedure gave roughly the pressure in dynes per square centimeter.

2. In the measurements of radiation pressure, it was easier to refer the intensity of the beam at each exposure to some arbitrary standard which could be kept constant than to try to hold the lamp as steady as would otherwise have been necessary. For this purpose, the bolometer at R (Fig. 3) was introduced, and simultaneous observations were made of the relative intensity of the reflected beam by the deflection of the galvanometer  $G_{2^{1}}$  and the pressure due to the transmitted beam by the deflection of the torsion balance. The actual deflection of the balance was then reduced to a deflection corresponding to a galvanometer deflection of 100 scale divisions. The galvanometer sensitiveness was carefully tested at the beginning and end of each evening's work. All observations of pressure were thus reduced to the pressure due to a beam of fixed intensity.

At each series of radiation pressure measurements, two sets of observations were made. In one of these sets, static conditions were observed, and in the other, the deflections of the balance due to short exposures were measured. In the static observations, each vane of the balance was exposed in turn to the beam from the lamp, the exposures lasting until the turning points of the swings showed that stationary conditions had been reached. The moment of pressure of radiation and gas action combined would thus be equal to the product of the static deflection and the constant of the balance. The torsion system was then turned through 180° by rotating the outside magnet, and similar observations were made on the reverse side of the vanes. All turning points of the swinging balance in these observations were recorded. From the data thus obtained the resultant of the combined radiation and gas forces could be determined for the time of every turning point. Every value was divided by the deflection at standard sensitiveness of the galvanometer  $G_2$  read at the same time and was thus reduced to a standard lamp. Results thus obtained, together with the ballistic measurements, showed the direction and extent of the gas action as well as its variation with length of exposure.

The reasons for reversing the suspension follow: The beam from the lamp, before reaching the balance, passed through three thick glass lenses and two glass plates. All wave-lengths destructively absorbed by the glass were thus sifted out of the beam by the time it reached the balance vanes. The silver coatings on the vanes absorbed therefore more than the glass. The radiation pressure was always away from the source irrespective of the way the vanes were turned, while the gas action would be exerted mainly on the silvered sides of the vanes.

At the close of the pressure and energy measurements, when the reflecting power of the silver faces of the vanes was compared with that of the glass-silver faces, the reflection from the silver faces was found very much higher than that for the glass faces backed by silver. This result was the more surprising because the absorption of the unsilvered vanes was found by measurement to be negligibly small.<sup>1</sup> This unexpected difference in reflecting power of the two faces of the mirrors prevented, the elimination of the gas action, by the method described, from being as complete as had

<sup>1</sup> Lord Rayleigh records a similar difference between the reflection from air-silver and glass-silver surfaces. Scientific Papers, Cambridge, II., pp. 538-539, 1900.

been hoped for. But by choosing a gas pressure where the gas action after long exposure is small, the whole gas effect during the time of a ballistic exposure may be so reduced as to be of little consequence in any case.

By exposing each of the vanes in turn and by reversing the suspension and averaging results, nearly all errors due to lack of symmetry in the balance or in the position of the light images with reference to the rotation axis, or errors due to lack of uniformity in the distribution of intensity in different parts of the image, could be eliminated.

The changing character of the gas action, both with time of exposure and gas pressure surrounding the balance vanes is well illustrated in eight series of static observations in which the glass faces of both vanes were exposed.<sup>1</sup> The results obtained on the two vanes were averaged and plotted as curves in Fig. 5, where static deflections due to combined radiation pressure and gas action are shown as ordinates and duration of exposure, in seconds, as abscissæ.<sup>2</sup> A horizontal line through the diagram gives the mean value of the moment of radiation pressure computed from the data in Table II. Decrease of the deflection with time indicates gas repulsion on the warmed silver faces and increase in deflection, gas suction. It will be seen from the curves that beginning at a gas pressure of 66 mm. of mercury, the gas action was repulsion changing to suction in passing from 19.8 to 11.2 mm. In the last two cases the total gas action is small. For lower pressures the suction increases to 0.05 mm. At a gas pressure of 0.02 mm. the gas action is again a strong. repulsion.

The curves indicate the existence of two gas pressures, at which the gas action in our arrangement of apparatus should be zero, one between 19.8 and 11.2 mm. and the other between 0.05 and 0.02 mm.<sup>3</sup> The former region was chosen for the ballistic measurements

<sup>1</sup>Observations were also made on the silver faces, but the gas action when the glass faces were exposed was considerably greater that for the silver faces, so the least favorable case is shown.

<sup>2</sup>Ordinates of the curves are proportional to moments.

<sup>3</sup>Crookes in his work with the radiometer discovered certain gas pressures for which the combined gas and radiation forces neutralized, but as he did not discriminate between forces due to radiation and gas forces his results were apparently capricious and his reasoning somewhat confused. See Phil. Trans., p. 519, 1875. and nearly all of the observations were made at a gas pressure of approximately 16 mm. Even for the two pressures where the decrease in the static deflection was most rapid, *i. e.*, at gas pres-

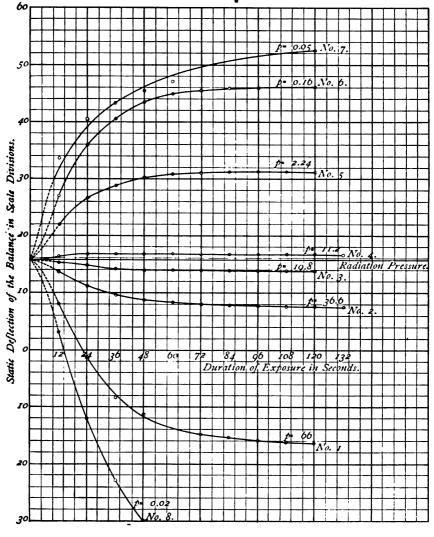


Fig. 5.

sures of 66 and 0.02 mm., the first throw was always in the direction of radiation pressure. The gas action is strongly influenced



by very slight changes in the inclination of the plane of the vanes to the vertical and also by any object introduced under the bell-jar anywhere near the vanes. For instance, a very considerable effect was observed when a small vessel of phosphoric anhydride was placed under the jar behind the vanes, though the nearest wall of the vessel was separated from the vanes by a distance of at least 3 cm.

During the observations, the polished silver coatings on the vanes deteriorated rapidly; new coatings rarely lasted for more than two evenings' work. As the balance had to be removed and the mirrors taken from the hooks, silvered, polished, and replaced a great number of times during the entire series of measurements, although great care was taken in setting the plane of the vanes vertical, it is not likely that precisely the same conditions for gas action were ever repeated. The principal value of the static results was in indicating favorable gas pressures for work, rather than affording quantitative estimates of the gas action in short exposures. The dotted parts of the curves are not based on results of observation and might perhaps have been omitted without loss.

It was plain, therefore, that further elimination of the gas action must be sought in exposures so short that the gas action would not have time to reach more than a small fraction of its stationary value. This led to the method of ballistic observations.

### THE BALLISTIC OBSERVATIONS.

In passing from the static to the ballistic observations it must always be possible to compute the static equivalent of the ballistic swings. Furthermore, the exposures should be made as short as possible without reducing the size of the swing below a value which can be accurately measured.

If the exposure lasts for one half the period of the balance, the deflection, if the gas action be small and the damping zero, is equal to  $2\theta$ , where  $\theta$  is the angle at which the torsion of the fiber will balance the moment produced by the radiation pressure. If the duration of the exposure be one quarter of the period of the balance, the angle of deflection is  $\theta \sqrt{2}$ . The deflection is thus reduced by 30 per cent., but the effect of the gas action is reduced in greater

proportion. It was decided therefore to expose, for six seconds, one quarter of the balance period. Neglecting the gas action, the equation  $^{1}$  of motion of the balance is given by

$$x\frac{\partial^2\theta}{\partial t^2} + 2\varepsilon\frac{\partial\theta}{\partial t} = -G\theta + L$$

where x = the moment of inertia of the torsion balance,

 $\varepsilon$  = the damping constant,

G = the moment of torsion of the fiber for  $\theta$  = 1 radian,

and L = the moment of the radiation force.

The solution of this equation is

$$\theta = \frac{L}{G} \left\{ 1 - e^{-\frac{\epsilon}{\kappa}t} \cos \sqrt{\frac{G}{\kappa} - \frac{\epsilon^2}{\kappa^2}t} \right\}$$
$$= \frac{L}{G} \left\{ 1 - e^{-\frac{\epsilon}{\kappa}t} \cos 2\pi \frac{t}{T} \right\}$$
(1)

the constants of integration having been determined from the condition that

$$\theta = \frac{\partial \theta}{\partial t} = 0$$
 when  $t = 0$ .

When

$$t = \frac{T}{4}, \quad \theta = \frac{L}{G}$$

and

$$\frac{\partial \theta}{\partial t} = \frac{L}{G} \left( \frac{\varepsilon}{x} e^{-\frac{\varepsilon}{\kappa}t} \cos 2\pi \frac{t}{T} + e^{-\frac{\varepsilon}{\kappa}t} \frac{2\pi}{T} \sin 2\pi \frac{t}{T} \right).$$
(2)

The light being cut off when t = T/4, the equation of motion becomes

$$x\frac{\partial^2\theta}{\partial t^2} + 2\varepsilon\frac{\partial\theta}{\partial t} = -G\theta \tag{3}$$

the solution of which is  $\theta = Ae^{-\frac{e}{\pi}t} \cos\left(2\pi \frac{t}{T} + a\right)$  where A and a

<sup>1</sup>We are justified in using quantitatively this equation, containing a damping term proportional to the velocity, because the amplitudes of the successive swings of the torsion balance, when no energy fell upon the vanes, were found experimentally to follow accurately the exponential law.



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can be determined by the conditions imposed by equation (2). Neglecting very small quantities, the value of the amplitude A is expressed by the equation

$$A = \frac{L}{G} \left\{ 1 + r + \frac{2}{\pi} r^{\dagger} \log \left( \frac{1}{r} \right) \right\}^{\frac{1}{2}}, \tag{4}$$

where r is the ratio of successive amplitudes of the damped vibra-If r = 1, that is if the motion is undamped,  $A = \sqrt{2L/G}$ . In tions. the partial vacuum used in the experiments (16 mm. of mercury, a value chosen from the curves in Fig. 5), r was found to be equal to 0.783; consequently

$$A = 1.357 \frac{L}{G}.$$
 (5)

From this it is seen that the total angle of deflection of the torsion balance in the ballistic measurements is equal to 1.357 times the angle at which the moment of the torsion of the fiber balances the moment of the radiation pressure.

The duration of exposure was always six seconds without appreciable error, but the period of the balance on account of slight accidental shifting of small additional masses upon the counterpoise weight  $m_s$  (Fig. 2), differed from twenty-four seconds sometimes by one per cent. It is necessary therefore to find the error in the deflection due to this variation in the period. This is done by making  $t = T/4 + \delta$  in equation (2) and in introducing the new conditions in equation (3). But it is simpler and sufficiently accurate to assume the motion as undamped. For this condition, the amplitude

$$A = \frac{L}{G} \left\{ 2 + 2 \sin 2\pi \frac{\delta}{T} \right\}^{\frac{1}{2}} = \sqrt{2} \frac{L}{G} \left( 1 + \pi \frac{\delta}{T} \right) \text{ nearly}$$

For T = 23.75 seconds,  $\frac{1}{4} = 5.94$  and  $\delta = 0.06$ . Hence

$$A = \sqrt{2} \frac{L}{G} (1.008).$$

If  $\delta = 0$ ,  $A = \sqrt{2} \frac{L}{C}$ , consequently an error of I per cent. in T causes an error of 0.8 per cent. in A.

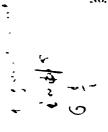
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To make sure that the observed radiation pressures depended only on the intensity of the beam, and were uninfluenced by the wavelength of the incident energy, the ballistic observations of pressure, the thermal measurements of intensity, and the determination of the reflection coefficients, were carried out for three entirely different wave-groups of the incident radiation. In the measurements designated "through air," no absorbing medium was introduced in the path of the beam between the lamp and the balance except the glass lenses and plates already mentioned. In the measurements "through red glass," a plate of ruby glass was put in the path of the beam between  $L_2$  and  $d_3$  (Fig. 3). For the observations

TABLE	IL

August 28. Light Pressure. Bal	listic Measurements. Air
--------------------------------	--------------------------

Surface.	Zero.	Throw.	Deflection.	Lamp.	Deflection	(Lamp 100)
ournace.	2010.	Intow.	Denection.	Demp.	E.V.	W.V.
EVC.	281.4	248.5	mm. 32.9	mm. 164.3	mm. 20.0	mm.
WVD.	281.4	313.9	32.4	164.5	20.0	19.7
EVC.	281.3	249.8	31.6	157.9	20.0	13.7
WVD.	281.5	310.5	29.0	147.0	20.0	19.8
EVC.	281.5	252.6	28.9	144.8	20.0	19.0
WVD.	281.5	309.6	28.1	141.8	20.0	19.8
EVC.	281.5	252.9	28.6	143.5	19.9	17.0
WVD.	281.5	309.3	27.8	140.4	15.5	19.8
-	1		1	Average	19.97	19.77
					$\frac{C_s+D_s}{2}=$	19.87
		M	lagnet Reversed	1		
EVDg	280.1	246.0	34.1	160.4	18.92	1.
WVC,	280.0	317.8	37.8	187.3		20.20
	279.8	247.2	32.6	170.8	19.20	
EVDg		010 8	34.3	169.4		20.25
E VDg WVCg	279.4	313.7	37.3			
•	279.4 279.1	313.7 248.9	30.2	161.1	18.80	
wvc,				161.1 161.6	18.80	20.35
WVCg EVDg	279.1	248.9	30.2		18.80 18.90	20.35
WVC, EVD, WVC,	279.1 279.0	248.9 311.9	30.2 32.9	161.6		20.35 20.20
WVCg EVDg WVCg EVDg	279.1 279.0 279.0	248.9 311.9 249.1	30.2 32.9 30.0	161.6 158.9		



No. 1.]





of Hg. Period 7. (1	Silver). (C	Sens. of Galvan'r. <i>G</i> Silver). (Glass).	/ = Lever Arm. cm.	$C_a + \underline{D}_a = P_a.$	$C_{\theta} + D_{\theta} = P_{\theta}$	P. Cor- rected for T=24".	$P_{\mu}$ Cor- rected for $T = 24''$ .	P.×G.	$P_{I} \times G_{I}$	Average.
	[734]	 '	.814	Average	Average = 18.88	Average	Average = 18.73	Average	= 16.89	16.89
	756	768	.814	19.67	16.94	19.51	16.81	18.12	15.86	17.00
	200	716	.814							
	682	207	.831	21.16	20.42	21.00	20.26	17.25	17.25	17.25
	684	684	.815		_					
	720	710	.815	19.34	19.98	19.18	19.82	16.93	17.28	17.10
	724	710	.823	20.16	19.40	20.00	19.25	17.60	16.61	17.10
15.7 23.82	721	716	.824	19.87	19.61	19.73	19.48	17.26	16.97	17.10
	712	701	.824	19.68	20.07	19.53	19.92	16.90	16.97	16.94
	718	713	.810	18.55	18.94	18.55	18.94	16.44	16.60	16.52
	692	672	808.	19.14	20.17	19.14	20.17	16.40	16.78.	16.59
	670	676	.812	20.96	20.02	20.81	19.87	17.17	16.54	16.86
	999	684	.816	21.32	20.27	21.16	20.12	17.27	16.87	17.07
	667	699	.816	20.76	19.80	20.60	19.65	16.84 ·	16.11	16.47
				1		1	Average,	17.11	16.71	$16.91 \pm 0.053$
1	duit the a	5	 	1		1			1	ŀ

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"through water cell," a 9-mm. layer of distilled water in a glass cell was placed in the path of the beam at the same point.

The separate observations entering into a single series of ballistic measurements and their treatment will appear from Table II., which is copied direct from the laboratory note-book and represents an average ballistic series. The designations  $EVC_a$ ,  $WVD_a$ ,  $EVD_a$ , and

			Through V	Vater Cell.			
Date.	$\frac{C_{\bullet}+D_{\bullet}}{2}$	$\frac{C_g + D_g}{2}.$	P. Corrected for $T = 24''$ .	$P_g$ Corrected for $T-24''$ .	$P_{\bullet} \times G_{\bullet}$	$\frac{P_{g}\times G_{g}}{l}$	P Average
June 20	18.62	17.10	18.46	16.96	17.14	16.00	16.57
July 25	19.00	20.10	18.85	19.94	15.82	16.74	16.28
* 26	18.03	19.39	17.89	19.33	15.80	16.84	16.32
Aug. 27	18.63	18.66	18.50	18.53	16.29	15.99	16.14
·· 29	18.25	19.02	18.10	18.87	15.68	16.06	15.87
Sept. 20	20.39	19.14	20.23	19.00	16.69	15.82	16.25
. 23	20.21	19.51	20.05	19.36	16.37	16.23	16.30
" 24	19.84	18.91	19.69	18.77	16.10	15.40	15.70
			Ave	rage	16.24	16.15	$16.20 \pm 0.060$
			Through F	ted Glass.			
June 23	19.99	18.40	19.83	18.26	17.05	16.06	16.56
July 25	20.70	20.94	20.54	20.77	17.24	17.43	17.33
Aug. 27	19.97	19.25	19.82	19.10	17.46	16.46	16.96
<b>''</b> 28	19.99	19.42	19.84	19.28	17.36	16.75	17.05
" 29	19.99	19.92	19.84	19.77	17.14	16.82	16.98
" 31	18.98	19.14	18.98	19.14	16.82	16.84	16.83
Sept. 20	21.00	19.97	20.83	19.82	17.19	16.50	16.84
" 23	21.48	20.34	21.31	20.18	17.39	16.92	17.15
" 24	21.00	19.68	20.83	19.53	17.03	16.03	16.53
	•	•	Ave	rage	17.18	16.65	16.91 + 0.05

TABLE IV.

Radiation Pressure. Ballistic Measurements.

 $WVC_g$ , mean that the vane C in the first case was on the east side of the rotation axis with its silver face toward the light. The subscript g signifies that the glass face of the vane was toward the light. The second column of the table gives the zero reading of

tion of the balance; the fifth, the ballistic deflection of the lamp galvanometer  $G_2$ . Columns six and seven give the balance deflection reduced to standard lamp.

The results of all the ballistic pressure measurements "through air," are collected in Table III. In the fourth and fifth columns two values are given for the constant of the lamp galvanometer  $G_{n}$ since reversing the magnet on the balance bell-jar to reverse the suspension within affected the constant of the galvanometer slightly. The values for the silver and glass faces forward were never the same. The subscripts show to which series, silver or glass, the constant belongs. The values of the lever-arm l of the balance in the sixth column, are obtained by measuring the distance between the centers of the images when on the east and west vanes (by the dividing engine  $T_2$ , Fig. 3) and dividing by two. The columns headed  $\frac{C_{g} + D_{g}}{2} = P_{g}$  and  $\frac{C_{g} + D_{g}}{2} = P_{g}$  are the average moments due to pressures for the silver and glass sides of the vanes respectively toward the light. The next two columns contain these moments corrected for a period of twenty-four seconds of the torsion The columns headed  $\frac{P_s \times G_s}{I}$  and  $\frac{P_g \times G_g}{I}$  are the correbalance. sponding forces reduced to standard sensitiveness, G = 1,000. The final column contains the averages of the two columns which pre-Table IV. exhibits corresponding data for "red glass" and cede it. "water cell." The air pressure, period of the balance, lever arm and galvanometer constants are those given in Table III. for the same date.

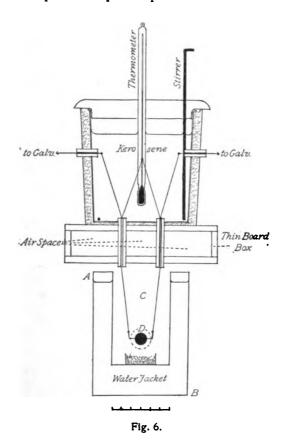
In these ballistic measurements the lamp reading was the throw due to an exposure of the light upon the bolometer for six seconds, but in the energy measurements the lamp reading was a stationary deflection due to prolonged exposure. To bring the pressure values into comparison with the energy measurements it is necessary to reduce the average of the quantities in the last column to pressures in dynes by multiplying by  $0.363 \times 10^{-5}$ , the torsion coefficient of the quartz fiber, and to reduce not only to a static deflection of the torsion balance but also to a static deflection of the lamp galvanometer  $G_{a}$ . The ratio of a ballistic to a static deflection 48

of the galvanometer  $G_2$  was obtained from a long series of lamp exposures. This ratio was found "through air" to be = 1.55; "through red glass" = 1.535; "through water cell" = 1.502. These differences are probably due not solely to the damping constant of the galvanometer but to the peculiar manner in which the bolometer was warmed up to its stationary conditions by the beam from the lamp. Applying these reduction factors to the averages in Tables III. and IV., we obtain the following results. The pressure of the standard light beam which has passed

(a) through air = 
$$16.91 \times \frac{1.55}{1.357} \times 0.363 \times 10^{-5}$$
  
=  $(7.01 \pm 0.023) \times 10^{-5}$  dynes;  
(b) through red glass =  $16.91 \times \frac{1.535}{1.357} \times 0.363 \times 10^{-5}$   
=  $(6.94 \pm 0.024) \times 10^{-5}$  dynes;  
(c) through water cell =  $16.20 \times \frac{1.502}{1.357} \times 0.363 \times 10^{-5}$   
=  $(6.52 \pm 0.028) \times 10^{-5}$  dynes.

THE ENERGY MEASUREMENTS.

Before rejecting the bolometer method used in the preliminary measurement of energy, a second bolometer of slightly different construction was tried; but the lack of uniformity of resistance, already mentioned, made its indications too uncertain for the present work. The radiant intensity of the beam used in the later experiments was determined by directing it upon the blackened face of a silver disc, weighing 4.80 grams, of 13.3 mm. diameter and of 3.58 mm. thickness, and by measuring its rate of temperature rise as it passed through the temperature of its surroundings. The disc was obtained from Messrs. Tiffany & Co. and was said by them to be 99.8 per cent. fine silver. Two holes were bored through parallel diameters of the disc, one fourth of the thickness of the disc from into the center of the disc. To insulate the wires from the disc, fine drawn glass tubes were slipped over them and thrust into the holes, leaving less than 2 mm. bare wire on either side of the junctions. The wires were sealed into the tubes, and the tubes into the disc by solid shellac. The tubes projected 15 mm. or more from the disc and were bent upward in planes parallel to the faces of the disc.



The general arrangement will be seen in Fig. 6. The disc was suspended by the four wires some distance below a small flat wooden box. On the box was fastened a calorimeter can swathed in cotton and filled with kerosene in which the constant thermojunctions were immersed. Copper wires soldered to the two ends of the thermo-electric series were brought out of the colorimeter, and the circuit was closed through 1,000 ohms. in series with the 500 ohms. resistance of galvanometer  $G_1$ . The thermo-junctions in the disc were in series, and as each junction was midway between the central plane of the disc and either face, it was assumed that when the disc was slowly warmed by heating one face the electromotive forces obtained corresponded to the mean temperature of the disc. One face of the disc was blackened by spraying it with powdered lampblack in alcohol containing a trace of shellac. This method was suggested by Professor G. E. Hale and gives very fine and uniform dead black coatings not inferior to good smoke deposits.

For the energy measurements the bell-jar and the torsion balance were removed from the platform P (Fig. 2) and a double-walled copper vessel, AB (Fig. 6), which served as a water jacket surrounding a small air chamber C, was mounted in the same place. A tube 2 cm. in diameter was soldered into the front face of the jacket to admit the light beam into the chamber C. This opening was covered by a piece of plate glass similar to the plates forming the larger windows in the bell-jar.

The needle system in  $G_1$ , a four-coil du Bois-Rubens galvanometer was suspended in a strong magnetic field so that its period was about four seconds. The system was heavily damped by a mica air-fan of large surface. The disc junctions and galvanometer responded quickly to the radiation, as was shown by the reversal of motion of the magnet system 1.2 seconds after the light was cut off from the disc when the latter was a few degrees above the temperature of the room.

(Concluded in next number.)

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# SOME OPTICAL PROPERTIES OF IODINE. III.

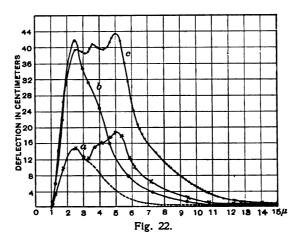
#### BY WM. W. COBLENTZ.

Since the publication of his previous work on iodine<sup>1</sup> the writer has been able to obtain very pure rock salt crystals from which cells could be made that were thin enough so that liquid substances could be explored up to  $16 \mu$ . At this point rock salt suddenly begins to absorb heavily<sup>2</sup> so that the exploration could not be extended beyond this point.

The cell walls were made by splitting the rock salt parallel to a cleavage plane. This gave thin plates that were quite plane, smooth, and of a finer polish than could be obtained by hand pol-In fact the surface thus obtained is not so easily attacked ishing. by moisture and is of far more service in all work like the present. To make a cell, a copper wire, varying from .16 to .3 mm. in diameter, was bent into a U shape, and coated with Lapage's glue. This was pressed between two plates of rock salt and permitted to dry. It was found that the substances investigated did not attack the glue after it had dried. The size of the cell was usually about  $1 \times 2.5$ cm. After it was filled, the top was covered with thick viscous glue. The cell was mounted on a heavy wooden block. This block moved in vertical ways, before the spectromoter slit, and had an opening about  $4 \times .5$  cm. cut in it, through which the transmitted energy passed and over which the cell was securely mounted. Α clear plate of rock salt was mounted directly below the cell, and all the remaining open spaces were covered with tinfoil. This arrangement prevented all radiation from getting into the radiometer except that which passed through the cell, or through the rock salt plate. A double-walled sheet-iron shutter was placed "heater" of a 110-volt Nernst lamp. In this work, however, a 90-volt storage battery system was employed, which gave a steady source of radiation.

The "heaters" consist of hollow cylinders of clay wound with platinum wire, the whole of which is covered with kaolin.

The extraordinary distribution of energy from these heaters is shown in Fig. 22. The first maximum is no doubt due to the hot



platinum wire, while the third maximum lies close to the absorption band of quartz found <sup>1</sup> at 5.3  $\mu$ . The minima lie close to the well-known atmospheric absorption bands of H<sub>2</sub>O and CO<sub>2</sub> found <sup>2</sup> 2.7 and 4.4  $\mu$ .

The suppression of the selective radiation at 5.3  $\mu$  and 8.0  $\mu$  is well illustrated in curve b. The film of Fe<sub>2</sub>O<sub>3</sub> was obtained by dipping the "heater" in a FeSO<sub>4</sub> solution, which was then oxidized by heating.<sup>3</sup> The dotted part of a indicates the probable radiation from the platinum wire which is wound on the heater. For curves a and b the spectrometer slit was .3 mm. wide. In actual work on absorption a wider slit (1 mm.) was used at the source, and a .4 mm. slit at the radiometer. Curve c represents the distribution of a for the latter case. With this slit-width the maximum of b is about 50 cm. deflection, but in the region beyond 8  $\mu$  the ordinates are not much higher than for the present curve. It will thus be seen that for work

<sup>1</sup> E. F. Nichols, PHys. Rev., 4, 1897.

<sup>2</sup> Paschen, Wied. Ann., 52, p. 223, 1894. <sup>3</sup> Paschen, Wied. Ann., 56, p. 762, 1895.



like the present, where large deflections are necessary, from 7 to 16  $\mu$ , the unmodified heater is the better. Curve *c* was obtained while finding the absorption of a certain compound, and is of interest, since, by its regularity, it shows the constancy of the radiation.

The radiation from this heater was found when covered with borax, also when a strip of mica .3 mm. in thickness was wound on it, but in neither case was the energy curve different from the original. The mica did not show emission minima at 8.4  $\mu$  and 9.4  $\mu$  as computed by Rosenthal.<sup>1</sup> However, the strip may have been too thin to show this effect.

The method of making observations consisted in noting the radiometer deflection for the transmission through the cell, and then, on raising the block until the rock salt plate was before the slit, that deflection was read. The ratio of the deflection through the cell to that through the rock salt gave the transmission immediately, and more accurately than by finding the absorption of the empty cell. The transmission of the solvent was first found, then, without disturbing the position of the mounted cell, that of the solution of the substance under investigation. It was found that if the cell was changed in its mounting, while making a series of observations, errors were introduced in the work. From the transmission through the solvent and the solution two curves are obtained, from which one can obtain the absorption due to the substance dissolved.

The exploration of the iodine solution in  $CS_2$  was undertaken to learn whether transparency continued in the region of 7.3  $\mu$  where solid iodine has a heavy absorption band. From the following curves it will be noticed that no such absorption occurs. In other words, the selective adsorption as well as general absorption, observed in solid iodine, disappears entirely when dissolved in carbon bisulphide or chloroform.

In the first part of this work mention was made of the well-known fact that iodine is brown in color when dissolved in alcohols, acids, ethers and aqueous solutions of metallic salts; that it imparts a red tint to benzine, toluene, etc.; and that in chloroform, carbon bisulphide, etc., the solutions are violet. Most of the above-named compounds have been investigated by Dutoit,<sup>2</sup> using a quartz prism.

<sup>8</sup> Dutoit, Bull. Soc. Vaudovise des Sci. Naturelle, 38, pp. 1–28, 1902.

<sup>&</sup>lt;sup>1</sup> Rosenthal, Wied. Ann., 68, p. 782, 1899.

#### W. W. COBLENTZ.

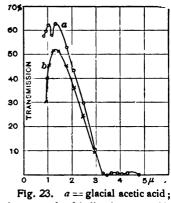
His explorations extent to 2.5  $\mu$ . He found a great similarity for the absorption of the brown solutions and also among those that are violet. He and the writer disagree however in that the former finds that the transparency of the brown and the violet solutions begins at about 1.8  $\mu$ , while the latter finds that the violet solutions become transparent at less than 1.4  $\mu$  and that the brown solutions continue to absorb beyond 2.5  $\mu$ . This is of minor importance, however, since Dutoit used sunlight for his source of energy, which was very unsteady, and may have introduced slight errors. Then

the purity of the materials must also be considered. For ordinary ethyl alcohol containing water the writer found transparency to begin at  $1.25 \mu$ (Fig. 10).

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For the present work absolut eethyl alcohol was selected to represent the brown, acetic acid the reddish-brown, and chloroform and carbon bisulphide the violet solutions.

In Fig. 23 is given the transmission curve of a layer of glacial acetic acid .18 mm. thick, and also the curve



b =sat. sol. of iodine in same acid.

for a saturated solution of iodine in this compound. The iodine

701 60 80 40 30 20 10 Б 6 /4 Fig. 24. a = ethyl alcohol; b = sat. sol. of iodine in C, H, OH.

absolute ethyl alcohol.

solution absorbs heavily throughout the whole region. Both become opaque at  $4 \mu$ , probably due to the presence of water.

With the present source of energy it is as difficult to work at I  $\mu$  as at I 2  $\mu$ , so that no at attempt was made to locate accurately the absoption band at I.I  $\mu$ . At this point a prism having greater dispersion is more useful.

In Fig. 24 is given the curve for a saturated solution of iodine'in Here the absorption is also heavy and

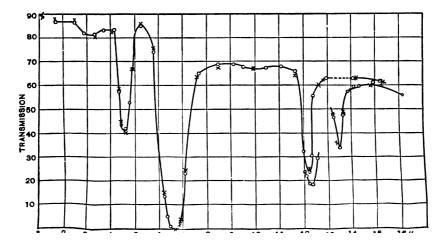
extends to  $3 \mu$ . Beyond this point the solution becomes transparent. Table I. gives the transmission for these two solutions.

Wave-		Sat. Sol.	Acetic	Sat. Sol.	t. Sol. Wave-		Cell .1	8 mm. Tl	nick.
lengths in µ.	Alcohol, C <sub>2</sub> H <sub>4</sub> OH	of Iodine in C,H,OH	Acid, C,H4O,	of Iodine in C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>		С,Н°ОН	C,H,OH + lodine.	С,Н.О,	C,H,O, + Iodine
.92	51		58	30	3.68	1.0	1.35	.34	0
.984	56.5	33	59	40	3.92	3.51		.2	0
1.06	61	44	62.3	45	4.05	6.97	6.8	0	0
1.16	68	43	57.5	52	4.35	18.8	19.2	.41	0
1.28	64	50	63	45	4.65	27.2	28.3		
1.46	63.2	54	1		4.8	27.6			
1.72	60.3	56.3	53	45.3	4.95	27.5	29.0	.42	0
2.03	52.5	50	43.4	36	5.28	25.1	26.1	ł	
2.50	41	38	30	24.7	5.53	21.2	22.0	0	0
2.93	19.5	16.5	10.5	9.8	5.80	11.5	13.8	1	
3.30	1.4	1.2	.2	0	6.03	.34	.61		
3.49	.34	I ↓	0	0	6.27	.25	.34		1
	1				6.78	00	00		

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Transmission through a saturated solution of iodine in absolute ethyl alcohol and in glacial acetic acid.

The violet solutions present a very different appearance. The curves for  $CS_2$ , and for a saturated solution of iodine in  $CS_2$ , in Fig. 25 coincide throughout the whole region from 1.5 to  $16 \mu$ . The



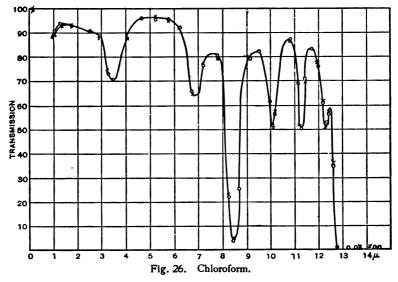


TABLE II.
Transmission through a saturated solution of iodine in CS <sub>2</sub> .

Wave-lengths	C8,	CS <sub>2</sub> + Iodine.	Wave-lengths	CS,	Cell 3 mm. Thick.
1B μ.			inμ.	-	CS <sub>2</sub> + Iodine
1.72	86.5	87.0	8.68	69.4	
2.50	86.8	87.6	9.12	69.2	
3.30	80.5	80	9.50	68.0	
3.68	83		9.88	67.5	67.4
4.05	83.4	83.7	10.50	68	
4.35	57.8	59.0	11.14	68	
4.48	43.3	46.2	11.17	66.7	64.4
4.65	41.6	40.8	11.95	32.6	
4.80	53.6		12.18	23.8	26.0
4.95	67.8	67.3	12.3	30.8	
5.28	85.0	85.6	12.4	57.0	
5.80	74.2	76.0	12.6	61	
6.27	14.0	14.3	13.0	63.2	62.5
6.40	5.4	1	14.1	62.7	62.8
6.50	1.15		Ce	ll .18 mm. t	hick.
6.60	.54	.48	13.32	47	48
6.78	.86		13.55	34	36
6.87	1.0		13.75	48	49
7.00	3.64	4.7	13.9	57.5	58
7.26	24	25.4	14.45	59	
7.80	65.3	66.3	14.8	59	60
8.25	66.4		15.3	59	
			16.1	56	1

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same coincidence occurs for the chloroform solution (Fig. 26), which has been indicated as absorbing a little at 1  $\mu$ . Here transparency begins at less than 1.4  $\mu$ . Tables II. and III. give the transmission for these two solutions.

T	T	TT.	
TABLE		II.	
TUDLE		***	

					Cell .16 m
Wave-lengths in µ.	Chloroform CHCl,	CHCl <sub>3</sub> + Iodine.	Wave lengths in $\mu$ .	снсі,	CHCl <sub>a</sub> + lodine
1.06	90.0	89.0	9.50	82.4	
1.28	93.4	92.8	9.88	61	61.2
1.72	92.3	92.2	10.02	51.7	51
2.50	90.3	90.0	10.18	56.4	57.3
2.93	88.4	87.6	10.5	82.0	82.5
3.3	73	73.3	10.8	87.4	85.6
4.05	87.2	87.5	11.14	<b>69.</b> 0	69.0
4.65	95.4	<b>95.3</b>	11.28	50	51
5.28	95.0	95.8	11.44	70.8	70
5.80	95.0	<del>94</del> .3	11.70	83.5	
6.27	81.4	81.0	11.95	77	79
6.78	65.4	64.9	12.18	61	61.5
7.26	76.8	77.2	12.30	53	50.5
7.8	80.2	79.8	12.4	56.5	58
8.25	22.4	22.8	12.6	35.0	36
8.48	4.4	4.03	12.8	00	00
8.68	25.5		13.0	00	00
9.12	79.5	80.5	14.0	00	00

Transmission through a saturated solution of iod	line in	chloroform.
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The carbon bisulphide curves show absorption bands with transmission minima at 3.1, 4.65, 6.7, 12.25 and 13.5  $\mu$ . The chloroform curves show minima at 3.35, 6.8, 8.5, 10.05, 11.35 and 12.26  $\mu$ .

#### SUMMARY.

The cause of the variation of the color of iodine in different compounds and solutions has been the subject of numerous investigations. Krüss and Thiele,<sup>1</sup> also Bechman,<sup>2</sup> have found that iodine solidified in various solvents, *e. g.*, ether, chloroform and benzine has a molecular weight =  $I_2$  for dilute solutions. Variations were irregular both for brown and for violet solutions. Concentrated solu-

<sup>1</sup>Krüss and Thiele, Zeit. Anorg. Chemie, 7, 25 (1894). Zeit. Phys. Chemie, Vol. VIII., p. 52.

<sup>2</sup> Bechman, Zeit. Phys. Chemie, Vol. V., p. 76, 1889.

tions usually gave high molecular weights. Gauthier and Charpy<sup>1</sup> found that brown solutions = I<sub>4</sub> but gradually break up to I<sub>2</sub> in becoming violet solutions, which is equivalent to iodine vapor. Paterno and Nasini<sup>2</sup> found I<sub>2</sub> for the molecular weight of iodine in acetic acid, for dilute solutions only, and a more complex structure in concentrated solutions. Finally Loeb<sup>3</sup> working on the vapor tensions of iodine solutions found I<sub>4</sub> in brown solutions, and I<sub>2</sub> to I<sub>3</sub> in violet solutions.

The most recent work on this subject is that of Lachman<sup>4</sup> who finds that iodine solutions have but two colors, red and brown, when made with pure solvents. "Saturated solvents give violet; solvents which have unsaturated character give brown solutions." The latter are oxygen compounds. Some of the brown solutions are known to contain periodides. Baeyer and Villiger<sup>5</sup> have recently demonstrated the additive powers of combined oxygen atoms in oxygen compounds. From these facts Lachman assumes that all brown iodine solutions contain some addition product (moleculesolvent +  $I_2$ ), while violet solutions contain simple iodine molecules. Since brown solutions tend to become violet when heated, and conversely, violet solutions become brown on being cooled; also, since heat produces dissociation, and cold induces association, the facts are in fair agreement with expectation.

Martens<sup>6</sup> has studied the influence as the absorption of C, S, Cl, Br and I in the ultra-violet. He found that the wave-length corresponding to the principal absorption band in the ultra-violet is approximately proportional to the square root of the atomic weight.

The present work deals with the absorption of iodine solution from the ultra-violet to  $16 \mu$  in the infra-red.<sup>7</sup> The brown solutions

<sup>2</sup> Paterno and Nasini, Berliner Ber., Vol. II., p. 2153, 1888.

<sup>4</sup> Lachman, A Probable Cause of the Different Colors of Iodine Solutions, Jour. Amer. Chem. Soc., Vol. XXV., No. 1, p. 50, 1903.

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<sup>&</sup>lt;sup>1</sup>Gauthier and Charpy, Compt. Rend , Vol. I., p. 189, 1890.

<sup>&</sup>lt;sup>3</sup> Loeb, Zeit. Phys. Chem., Vol. VII., p. 606.

<sup>&</sup>lt;sup>6</sup> Baeyer and Villiger, Ber. d. Chem. Ges., 34, 2679 (1901).

<sup>&</sup>lt;sup>6</sup> Martens, Deutsch. Phys. Gesell., Verh. 4, p. 138, 1902.

<sup>&</sup>lt;sup>7</sup> The refractive indices for wave-lengths from 9 to  $12 \mu$ , used in this work, were the

were found to be quite transparent at the red end of the spectrum, , and to absorb heavily in the violet. The violet solutions absorb heavily in the visible, and transmit violet and all the infra-red beyond  $1.2 \mu$ .

A study of the absorption spectra of iodine in solution does not tell us the exact nature of the structure of iodine in these solutions, but from the work just quoted it must be conceded that this very different behavior of the brown and violet solutions is due, in part at least, to the variation in the molecular structure of iodine when dissolved in these two classes of solvents. Few substances have been so thoroughly investigated, yet from a chemical as well as a physical standpoint, the question of the exact composition of iodine in solution remains unsolved.

# PHYSICAL LABORATORY OF CORNELL UNIVERSITY,

#### February, 1903.

did not. Since then it has been found that these observed indices in Vol. 60 are wrong or misprints, and that the correct values are given in an inconspicuous, unindexed notice in Wied. Ann., 61, p. 224, 1897, which has escaped the attention of at least one person besides the writer. The whole is unfortunate. As a result of this the wave-lengths are too large by .29  $\mu$  at 9  $\mu$ , by .4  $\mu$  at 10.57  $\mu$  and by .16  $\mu$  at 13  $\mu$ , beyond which they remain almost as plotted. Furthermore the correction for lack of minimum deviation is nowhere greater than .08 $\mu$  instead of the largest value given in the table. A final correction will be given in the future. April, 1903.

#### NEW BOOKS.

A Manual of Physical Measurements. By JOHN O. REED and KARL E. GUTHE. Ann Arbor, Michigan, George Wahr, publisher, 1902. Pp. 185.

This manual of laboratory physics is one of the class designed primarily to satisfy the requirements of the laboratory where it was prepared. It describes the work required of students in physics and electrical engineering in their first course in the physical laboratory at the University of Michigan. It is a laboratory manual in the proper sense, being planned for the student's use in work supplementary to a course of lectures and recitations in theoretical physics.

The book contains brief general instructions upon the objects and methods of laboratory work and computation; it describes sixty-six exercises in one hundred and seventy-five pages, and there are ten tables of constants besides tables of four-place trigonometric functions and logarithms. The problems are distributed as follows: Twenty in mechanics, two in sound, five in heat, ten in light and twenty-eight in electricity. The criticism might be made upon this selection that there are too few exercises in mechanics, sound and heat.

The chapter on elasticity contains seven of the twenty problems in mechanics, and fills nearly half of the space allotted to this section. The treatment is excellent, but its fullness makes more apparent, by contrast, the lack of completeness in the other parts.

The optical measurements include the curvature and focal lengths of lenses, the magnifying power of a telescope, index of refraction with the microscope and the spectrometer, and wave-length with a transmission grating. The five exercises in heat are upon the fixed points of a thermometer, the water equivalent of a calorimeter, specific heat of a solid, and the heat of fusion and heat of vaporization of water. In sound there are only exercises on the velocity of sound by Kundt's method, and a graphic method for rating a tuning-fork. The twenty-eight exercises in electricity cover in an acceptable manner the usual laboratory exercises of this class, making this section the most satisfactory, because of its completeness.

The instructions give such theoretical discussions as experience shows are necessary to refresh the memory of the student. The practical operations are described methodically, not simply enumerated. A number of general descriptions are given upon important subjects such as length, time and mass, and electrical units and standards. Often the instructions seem to lack thoroughness, but since the authors state "the book being designed for beginners, makes no claim to completeness either in subject matter or in exposition," this cannot be held as a valid criticism.

Of positive errors not many have been noticed, but there is one that must be referred to at length. The correct formula is given for computing the probable error of a series of observations, then the following explanation is made. "If e be the probable error of a set of readings, a the average, and x the true value of the reading sought, then

a+e>x>a-e;

which means that the true value of x lies between the mean *plus* the probable error and the mean *minus* the probable error." This erroneous idea of probable error is sometimes met with, but to find it so explicitly stated in a text-book is indeed serious. It is necessary to call the student's attention to the fact that the probable error is not a limiting value such that there is no probability of a greater error; and that it is a quantity such that in a large series there are certain to be just as many errors greater than it, as there are smaller ones. The real magnitude of the error such that there is only one chance in a thousand of a greater error, is nearly five times as large as the probable error.

A graphical method is given for correcting calorimeter observations for radiation, which is both incorrect and inconsistent with itself. Under thermometry it is stated that the fixed points of a thermometer should be frequently determined. In good practice the boiling point will never be determined more than once, and this information should be given to the student. The instructions are first to determine the ice point, and then the steam point; after this the ice point is to be redetermined. But the description does not mention any use to be made of the redetermined ice-point, while this is really the only determination that should be used in finding the fundamental interval.

There are several statements to which one might take exception; such, for instance, as that aluminum is the best material for the cup of a calorimeter, and that the most accurate method for measuring resistances is by means of the Wheatstone bridge, and that the proper method for focusing the telescope of a spectrometer is to remove it from its carrier and sight it on the moons of Jupiter or the planet Venus.

There appears to be no use made of the table of atomic weights, while its room might well be taken for a table of temperature corrections to barometric readings. Forms of record are given for every exercise. These are not always systematic, and sometimes degenerate into a list of quantities to be observed, and they even contain a list of logarithms required. The reviewer believes that such forms are detrimental.

The typography is good except in one particular; letters used as symbols are given in ordinary roman characters instead of the universal italic form. This makes reading somewhat difficult. Many of the cuts are not as good as they should be, and the same may be said of the printing and stitching.

Perhaps it is not a reviewer's province to say what a book should be but rather to learn whether it is what its author intended it to be. As compared with other books of the class to which it avowedly belongs, this one, except as noted above, is unusually satisfactory. The selection and arrangement of exercises covers the subject in a well-balanced, though brief, manner, forming a coherent and logical course, such as has been proved to be generally acceptable. No innovations in method or apparatus are exploited. While greater precision of detail might seem desirable to many, yet for a short course (this one is stated to be for forty exercises of two hours each) given to general college classes, and for one in which elaborate apparatus is not used, this book is one of the most satisfactory manuals that has been prepared.

DAYTON C. MILLER.

# The Physical Papers of Henry Augustus Rowland. Baltimore, The Johns Hopkins Press, 1902. Pp. xii + 704.

The papers of the late Professor Rowland have been collected into a volume by a committee of the faculty of the Johns Hopkins University under the editorial supervision of Professor Ames. The volume opens appropriately with the sympathetic and appreciative address by President T. C. Mendenhall which was delivered in commemoration of Rowland's services to science, at Baltimore in 1901 and which forms a fitting introduction to the scientific papers. The book closes with a description by Professor Ames of the Rowland dividing engines with an admirable set of drawings showing in detail the mechanism of these remarkable machines.

Rowland's scientific work is too well known to demand any detailed comment here. Some readers will doubtless regret the decision of the committee of editors to omit the tables of standard wave-lengths to the preparation of which he devoted ten years of his life. They would have added somewhat to the bulk of the already large volume but they would at the same time have added greatly to its usefulness. As it stands however this collection of physical papers is an imposing monument to the genius of the author and it will find its proper place upon our shelves, a No. 1.]

worthy companion piece to the collected memoirs of Maxwell, Tait, Rayleigh and Kelvin.

E. L. N.

Verhandlungen der ersten internationalen seismologischen Konferenz zu Strassburg. Ergänzungsband I., herausgegeben von G. GERLAND. Leipzig, Engelmann, 1902. Pp. viii + 439.

The first supplementary volume of the international seismological conference at Strassburg is devoted to geophysics. It contains in addition to descriptions of the systematic study of earthquakes, a number of papers of more direct interest to the physicist.

Professor Laska contributes a study of those peculiar movements of the horizontal pendulum which, in contradistinction to the temporary pulsations ascribable to the usual earthquake disturbances, are of long-continued duration; lasting in some instances without interruption for months at a time. Experience shows that certain pendulums are particularly subject to this class of disturbance while others at the same station remain in comparative quiescence. The author ascribes this peculiar behavior to the fact that various layers of the earth's crust transmit seismic waves of some given length freely and suppress others. When a pendulum happens to be in tune with the layer upon which it is placed, it in turn responds to the waves transmitted by this layer while other equally sensitive pendulums remain at rest. Such pendulums show little additional disturbance during times of earthquake while those commonly at rest, may respond to the earthquake waves to a marked degree.

Laska finds an intimate connection between barometric pressure and these disturbances. He considers them on the other hand to be uninfluenced by local winds and he calls attention to an as yet unexplained coincidence between magnetic storms which disturb the compass needle and movements of the horizontal pendulum.

A paper by Professor Straubel of Jena, deals with the means of illuminating chronograph sheets for the photographic registration of deflections. He favors the combination of a concave mirror behind a linear source of light, a diaphragm in front of the same and a cylindrical lens by means of which an image of the diaphragm is thrown upon the sensitized surface.

The specific intensities of the sources of light commonly available for such purposes were found to be as follows:

Petroleum lamp, .036; acetylene flame, .07; Welsbach mantle, .10; glow lamp, .80; Nernst lamp, 3.0.

An investigation of the advantages of a quartz-fluorite system as compared with optical glass, undertaken by Dr. Lehmann at the request of the author, showed that the actinic action upon the photographic surface

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#### NEW BOOKS.

for those portions of the spectrum in which the glass exerts strong absorption, is so slight when any of the sources of light mentioned above are used, that nothing is to be gained by the substitution of quartz and fluorite for glass.

#### E. L. N.

#### Galvanic Batteries: Their Theory, Construction and Use. By S. R. BOTTONE. Whittaker & Co., London and New York, 1902. Pp. 376.

This book contains ten chapters. The first gives a brief account of the work of Sulzer, Galvani and Volta. The next four describe, in an elementary manner, the principles involved in the operation of a galvanic battery and explain the meaning of the more common electrical and mechanical units. They also treat of the various methods of connecting cells and differentiate between primary and secondary batteries. The sixth chapter covers 230 pages or over two thirds of the book. Its subject is "Tabulation of the Different Cells." It constitutes the most important part of the book and the author's idea in preparing it is evidenced in the preface where he says : "A description of every known battery of any practical use is given, along with data as to E.M.F., internal resistance and adaptability to particular requirements." There certainly is a large number described. Some of them have demonstrated their usefulness by surviving their inception. Commercial requirements, however, have standardized primary battery practice to such an extent that but few types are necessary to meet the various demands. This part of the book is interesting to read and will be of value to those who are developing primary cells. The list is not, however, complete. Two important omissions are descriptions of the Reichsanstalt pattern of standard Clark cell and of the Carhart low temperature-coefficient standard cell. rest of the book is devoted to dry batteries, choice of batteries and details and construction of the more useful cells and storage batteries. The book has 144 illustrations and a complete index.

SAMUEL SHELDON.

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August, 1903.

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## ТНЕ

# PHYSICAL REVIEW.

# A SPECTROPHOTOMETRIC STUDY OF THE LUMI-NOUS RADIATION FROM THE NERNST LAMP GLOWER UNDER VARYING CURRENT DENSITY.

BY LEON W. HARTMAN.

THE character of the luminous radiation from different sources of light has occupied the attention of physicists for many years. The numerous problems related to this subject which have been studied represent widely diversified interests and extend over a wide range of investigation. Thus, in radiation, for example, the luminous radiation and the radiant efficiency of the magnesium light were studied by Rogers;<sup>1</sup> the luminous radiation from the Auer mantle was studied by Miss Hill;<sup>2</sup> that from zinc oxide by Nichols and Snow;<sup>3</sup> that from the lime light by Pickering,<sup>4</sup> by Nichols and Franklin,<sup>5</sup> and by Nichols and Miss Crehore;<sup>6</sup> the total radiation and the radiant efficiency of the mercury arc were studied by Arons,<sup>7</sup> Geer,<sup>8</sup> and Geer and Coblentz;<sup>9</sup> that from platinum has been studied by numerous investigators, among whom mention may be made of

<sup>&</sup>lt;sup>1</sup>Rogers, Am. Jour. Sci., 43, p. 301, 1892.

<sup>&</sup>lt;sup>2</sup> Nichols, Lab. Manual, 2, p. 373, 1894.

<sup>&</sup>lt;sup>3</sup> Nichols and Snow, Phil. Mag., [5], 32, p. 401, 1891.

<sup>&</sup>lt;sup>4</sup>Pickering, Proc. Am. Acad. Arts and Sci., 15, p. 236, 1880.

<sup>&</sup>lt;sup>5</sup>Nichols and Franklin, Am. Jour. Sci., 38, p. 100, 1889.

Magnus,<sup>1</sup> Violle,<sup>2</sup> Draper,<sup>3</sup> Nichols,<sup>4</sup> Chatelier,<sup>5</sup> Becquerel,<sup>6</sup> Crova<sup>7</sup> and Zöllner.<sup>8</sup>

The radiation from heated pigments was studied by Nichols and Snow.<sup>9</sup> The radiation from different forms of carbon has been thoroughly and carefully studied by Weber,<sup>10</sup> Schumann,<sup>11</sup> Nichols and Franklin,<sup>12</sup> Nichols,<sup>13</sup> Blaker,<sup>14</sup> Stewart,<sup>15</sup> Janet,<sup>16</sup> Le Chatelier <sup>17</sup> and others. In perusing some of the work mentioned above, it occurred to the writer that a study of the radiation from the rare-earth oxides used in the "glower" of the Nernst lamp would be of theoretical interest and of practical importance. In a paper on the behavior of these "glowers" when carrying an electric current,<sup>18</sup> mention is made of a spectral and bolometric study of the radiation from these luminous sources, but apparently no work was done in this direction. Inasmuch as no published work has appeared on this phase of the radiation from the Nernst lamp glower, it was decided to investigate this problem.

Inasmuch as no spectrophotometer was available for this work, a Kirchhoff spectrometer having a collimator with two unilateral micrometer slits was adapted for the purpose. This instrument has been described elsewhere.<sup>19</sup> This spectrometer has a broad circular horizontal plate of metal mounted upon a massive hollow cast-iron

<sup>1</sup>Magnus, Ann. der Phys., 124, p. 476, 1865.

<sup>2</sup> Violle, C. R., 88, p. 171, 1879; 92, pp. 866, 1204, 1881; 95, p. 163, 1887; 94, p. 734, 1892.

<sup>3</sup> Draper, Phil. Mag., [3], 30, p. 345, 1847.

<sup>4</sup> Nichols, Am. Jour. Sci., 18, p. 446, 1879.

<sup>5</sup>Chatelier, C. R., 114, p. 470, 1892; Bul. Soc. Chim. Paris, 47, p. 42, 1887.

<sup>6</sup>Becquerel, Annals de Chem. et de Physique, [3], **68**, p. 47, 1863; C. R., 55, p. 876, 1863.

<sup>7</sup>Crova, C. R., 57, p. 497, 1878.

<sup>a</sup> Pogg. Ann., 100, p. 381, 1857; 109, p. 256, 1869.

<sup>9</sup> Nichols and Snow, Phil. Mag., [5], 32, p. 401, 1891.

<sup>10</sup>Weber, Wied. Ann., 32, p. 256, 1897; PHYS. REV., 2, pp. 112, 197, 1894.

<sup>11</sup> Schumann, Electrotech. Zeitschr., 5, p. 220, 1884.

<sup>12</sup> Nichols and Franklin, Am. Jour. Sci., 38, p. 100, 1889.

<sup>18</sup> Nichols, Proc. Am. Acad. Arts and Sci., 37, p. 73, 1901.

14 Blaker, PHYS. REV., 13, p. 345, 1901.

<sup>15</sup> Stewart, PHYS. REV., 13, p. 257, 1901; 15, p. 306, 1902.

<sup>16</sup> Janet, C. R., 123, p. 690, 1896; 126, p. 734, 1898.

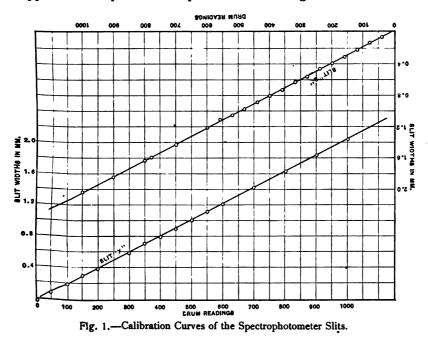
<sup>17</sup> Le Chatelier, Jour. de Phys., [3], 1, p. 203, 1892.

18 Nernst and Wild, Zeitschr. für Electrochemie, 7, p. 373, 1900.

<sup>19</sup> Wüllner, Lehrbuch der Experimentalphysik, Bd. 4, p. 168, 1899.



column, which in turn is supported by three massive feet. Mounted upon this plate is the collimator and the swinging arm which supports the observing telescope. This arm is rigidly attached to a revolving pivot passing downward through the vertical axis of the instrument. In a vertical plane beneath the plate is mounted a plane mirror which is rigidly attached to the pivot of the telescope arm; thus when the telescope is rotated about its axis, the mirror rotates about the same axis. Through an opening in the cast-iron support of the spectrometer plate a beam of light from an illumi-



nated scale falls upon the mirror and is reflected into another observing telescope which is rigidly attached by metal supports to the lower surface of the circular plate as shown in Fig. 4.

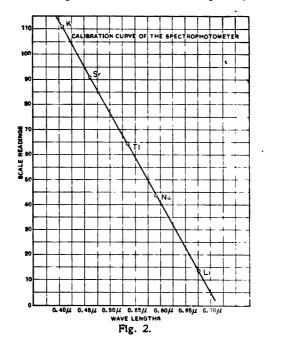
The train of glass prisms belonging to the instrument was removed and replaced by a Rowland plane grating, having 14,437 lines to the inch, ruled on speculum metal. This grating was mounted in

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of the spectrum was secured, and a normal spectrum and a straight line calibration curve were obtained. The collimator slits were then removed and calibrated under a high power microscope mounted on a Hilger dividing engine. Proper precautions were taken to avoid any error in measurement due to the "back lash" of the screw of the dividing engine or of the screws of the slits. The calibration curves given in Fig. 1 show that the screws of the slits are remarkably uniform and perfect. In Fig. 1 slit S refers to the slit which throughout was used with standard No. 1; slit  $X_{i}$ , therefore, was the slit before which was placed the Hefner lamp, the Nernst lamp and standard No. 2. In front of the upper slit of the collimator a totally reflecting prism was then mounted upon a blackened brass arm which swung about a vertical axis. By means of a screw adjustment this prism could be raised or lowered at will. The position of the prism in front of the collimator can be seen in Fig. 4. After remounting the slits the collimator and telescope were adjusted for parallel light. The collimator was then turned so that its axis passed normally through the vertical axis of the spectrometer, after which it was securely clamped in position. Thus, a beam of light passing through the collimator fell upon the middle portion of the Rowland grating. The observing telescope of the spectrometer, the ocular of which contained the cross-hairs and an adjustable slit so that only a narrow band of the spectrum could be observed at once, was then rigidly attached to its arm so that it had motion on this arm only in a vertical plane. As was noted above, this arm was attached to the axis of the instrument about which it could be swung in a horizontal plane. Thus the center of the grating was in the axis of rotation of the telescope. The spectrometer was then mounted in a dark room where this investigation was conducted. After the grating was adjusted so as to give a suitable intensity and dispersion in the spectrum of the first order, a scale divided into millimeters was suspended in front of the spectrometer mirror, by means of cords from one corner of the dark room. The spectrometer was then calibrated, by reference to the lines produced by vaporizing various metal salts in a Bunsen flame placed in front of the collimator slits. The calibration curve thus obtained was a straight line. The dispersion

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2. n was found to be sufficient to separate appreciably the two sodium lines and a difference of  $0.001 \mu$  was found to be equivalent to about 3.6 mm. on the scale. By virtue of certain changes that were made before any observations were taken several calibrations of the spectrometer were necessary, the final one of which is given in Fig. 2. The only difference found in these curves was a definite vertical shift throughout the whole length of the curve. Hence the calibration of the instrument could be tested at any time by reference to a sodium flame. As a precaution this was frequently done. As a

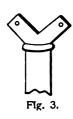


matter of fact the dark room in which this work was carried out was kept locked and no one but the writer was supposed to enter it, so that once adjustments were finally made, they were not disturbed by any one outside. The spectrometer observations and scale readings therefore never showed an appreciable difference from the calibration curve readings.

As a standard source of light an acetylene flame burning under constant pressure was used. The acetylene was produced in a Colt Automatic Acetylene Generator, in which finely divided calcium

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carbide was automatically dropped into water. The gas thus generated was passed over into a gasometer whence it was conducted through a pressure regulator of the Moler pattern<sup>1</sup> into the dark room. By means of a glass Y placed in the line of gas tubing leading from the regulator, one branch of which lead to a U-tube water manometer, while the other branch lead to the burner, the gas pressure at the burner could be observed at will through a telescope placed near the observer at the spectrometer. To prevent evaporation from the manometer, the open end of the U-tube was closed with a cork having a small groove along the side. The acetylene was burned in a No. 4 Naphey burner<sup>2</sup> of the type shown in Fig. 3. In front of the flat flame of this burner and parallel to its plane was mounted a sheet of blackened tin containing a circular diaphragm 7.94 mm.<sup>3</sup> in diameter so that the opening was opposite the most uniform portion of the flame. This burner with dia-



phragm was then mounted to the right of the collimator slits with the sheet of tin facing the totally reflecting prism and its plane 10 cm. from the face of the prism. When this diaphragmed source of light was placed in the proper position before the reflecting prism, the burner was rigidly clamped in place and remained undisturbed throughout the whole investigation. It

has been shown that such a source of light under constant pressure gives an intensity which remains uniform <sup>4</sup> and is therefore suitable for this investigation.

The Nernst lamp used was a 104-volt A. C. lamp. The "holder"<sup>b</sup> of the lamp was removed and the lamp was mounted on a support at a proper height so that the glower was horizontal and 100 cm. in front of the uncovered collimator slit. In series with the lamp was a rheostat (R) and a new accurately calibrated Weston A. C. ammeter (A), and to the platinum terminal wires of the glower were soldered the terminal wires of a recently calibrated Weston D. C. and A. C. voltmeter (V). Thus the voltages given in the data are

<sup>1</sup> Nichols, Jour. Frank. Inst., 150, p. 359, 1900.

<sup>2</sup> A No. 4 Naphey burner is rated to burn one cubic foot of gas per hour.

 $^{3}_{16}$  inches = 7.94 mm.

<sup>4</sup>Nichols, Jour. Frank. Inst., 150, pp. 360, 386, 1900.

<sup>5</sup> The Nernst lamp and its parts have been fully described by Mr. A. J. Wurts, Trans. Am. Inst. Elect. Eng., 18, p. 545, 1901.



those between the ends of the glower under varying current. It may be noted in passing that the lamp in this horizontal position was not entirely automatic, but inasmuch as the holder of the lamp had been removed, the heating circuit in each case was closed by hand, and when the glower became conducting the heating circuit was opened automatically. The arrangement of the apparatus is shown in Fig. 4.

In order to secure an alternating current of constant potential, a direct current of 110 volts was connected to the terminals of a 110volt storage battery, and from the leads of the battery a line was run to the terminals of a motor belted to a line of shafting, from which was furnished the power to run the alternator and its exciter. Thus the A. C. voltage could be kept constant at any desired value

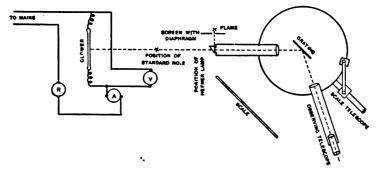


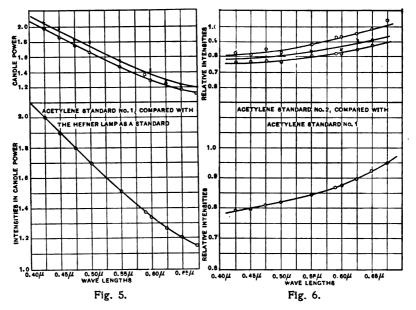
Fig. 4.-Diagram of Apparatus.

below its maximum. When the maximum value was reached, current was taken from the city A. C. mains which entered the laboratory.

To obtain results in terms of definite known units the Hefner-Altneck standard lamp<sup>1</sup> was used. That is, the diaphragmed acetylene flame used as a standard was determined in terms of the Hefner standard. This had previously been done, and the results obtained here are concordant with the earlier measurements. As has been pointed out it is desirable to compare the acetylene flame with the Hefner standard since in the latter the flame is produced by the combustion of a fuel of definite chemical composition under very nearly constant conditions.<sup>2</sup>

> <sup>1</sup>Zeitschr. für Instrumentenkunde, 13, pp. 257–265, 1893. <sup>2</sup> Nichols, Jour. Frank. Inst., 150, p. 371, 1900.

The method of taking the observations was as follows: Ten centimeters in front of the uncovered collimator slit, the Hefner lamp was adjusted in position. The lamp was allowed to burn twenty minutes or half an hour and then adjusted to the proper flame height, after which readings at various points in the spectrum were taken. Throughout the whole work eight or ten, and sometimes thirty or forty, readings were taken at each setting of the telescope. The mean of these readings was then taken for the position in question. Thus on different days a number of such curves were taken with the Hefner lamp, and the curves thus de-



termined were found to agree so closely that a mean curve of the two agreeing most closely was taken. The latter is shown in Fig. 5. The data for these curves is given in Table I.

Fifty centimeters in front of the collimator slits was temporarily mounted another No. 4 Naphey burner having a blackened screen mounted in front of it with a circular diaphragm of exactly the same size as that used with the burner previously mentioned. This acetylene source is called standard No. 2; the former acetylene source, standard No. 1. The spectrophotometric curve of standard No. 2 in terms of No. 1 was then determined. This curve, shown

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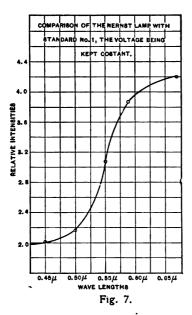
	-	Mean Ratio of Intensities in Candle	Curves.	2.010	1.900	1.800	1.701	1.515	1.372	1.340	1.268	1.205	1.147
	7.4 cm. 33.5°C. 15.8°C.	C. P.		1.98	1.86	1.752	1.658	1.480	1.378	1.30	1.262	1.175	1.125
	~:ea	tio of naities in finers.	Ra Iore H	2.30	2.16	5.0 <b>7</b>	1.925	1.72	1.603	1.51	1.470	1.368	1.304
	2~~	lidthe am.	SB	0.287	0.287	0.287	0.287	0.287	0.287	0.287	0.287	0.287	0.287
mþ.	Barometric Pressure = Psychrometer Readings	Slit Widths in mm.	S1	0.125	0.133	0.141	0.149	0.167	0.179	0.190	0.195	0.210	0.220
lefner La	Baromet Paychrol	dings of neter.	SR	150	150	150	150	150	150	150	150	150	150
1 with H		Drum Readings of Micrometer.	Sı	75.25	78.88	82.40	86.00	94.75	102.13	104.9	107.4	114.4	118.8
mdard No. 1		tio of C. P.	a atai at	2.05	1.99	1.82	1.80	1.54	1.39	1.42	1.272	1.242	1.052
Compurison of Standard No. 1 with Hefner Lamp.	= 7.4 cm. = 33.2°C. = 15.5°C.	tio of nsities in sfaers,	ag erai era	2.37	2.30	2.10	2.08	1.78	1.605	1.640	1.470	1.435	1.217
Compu	1.4  mm. $P = 7Dry Bulb = 2Wet Bulb = 1$	Widths mm.	SH	0.287	0.287	0.287	0.287	0.287	0.287	0.287	0.287	0.287	0.287
1	, v <b>∂</b> ~~~	Silt Widths in mm.	S,	0.121	0.125	0.1365	0.1380	0.1610	0.179	0.176	0.195	0.200	0.236
	c Pressure ster Readi	dings of leter.	SH	150	150	150	150	150	150	150	150	150	150
	Barometric Pressure = 764 Psychrometer Readings {	Drum Readings of Micrometer,	S.	73.44	74.90	80.11	81.11	92.00	99.87	98.30	107.40	109.70	126.25
1		ave- ethe		425 μ	450 µ	475 μ	500 μ	550 µ	589 µ	600 μ	625 µ	650 µ	675 "

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in Fig. 6, is the mean of several sets of independent observations taken on different days. This curve was obtained for the purpose of eliminating the absorption of the totally reflecting prism, which was not only marked but was also selective, as will be seen by referring to Fig. 6. Obviously, therefore, when the Nernst lamp is compared with a bare acetylene flame the results will be different from those obtained in the comparison with standard No. I in which the use of the reflecting prism is necessary.

Lastly, the Nernst lamp glower while carrying currents of different densities was compared spectrophotometrically with standard No. 1. At each observation throughout the whole series the current strength and the gas pressure were observed to see that they remained constant while a given set of observations was being taken.



From eight to ten readings were taken for each point on the curve. In some cases as many as fifty observations were made for each point and then the mean was taken. The gas pressure was most conveniently kept constant at 7.4 cm. of water pressure.

In using the Hefner-Altneck lamp corrections for humidity and barometric pressure according to Liebenthal's method<sup>1</sup> were made. Humidity was determined by observing the wet and dry bulb psychrometer and by using the values of vapor pressure obtained from Regnault's measurements.<sup>2</sup>

In taking the measurements on the Nernst lamp the first observations were made on another glower than on the one used throughout the series of measurements given in this paper. It was the original intention to obtain the spectrophotometric curves with the voltage maintained constant for a given set of observations. This, however, proved to be unsatisfactory. As an

<sup>1</sup>Liebenthal, Electroteck. Zeitschr., 16, p. 655, 1895.

<sup>2</sup>Hempel's Gas. Analysis. Translated by Dennis, pp. 255, 373-4, 1892.

	- <i>d</i> (I)	(1) $P = 7.4$ cm	•		•93		(a) $P = 7.4$ cm	· 7.4 cm.				(3) P=	(3) P = 7.4 cm.		.85. 1	M can
Wave- Lengths.	of Micr	Drum Readings Micrometer.	Slit V in J	Silt Widths in mm.	to olf#S elfienst	Drum Readings of Micrometer.	n Readings icrometer.	Slit Widths mm.	Iths in	o oitaX itiaast	of Micr	Drum Readings Micrometer.	Slit Width in mm.	Widths mm.	o oita9 itizaști	Relative Intensity of 1, 3 and 3 from
•	s,	S.	S	S.	aI	S <sub>1</sub>	S.	s,	S.	al	s,	.°°	s,	s.		Curves.
λ=0.425 μ		1				89.30	100	0.152	0.183	0.830	82.6	8	0.141	0.183	0.770	0.793
λ=0. <b>450</b> μ	86.6	10	0.150	0.183	0.820	86.33	8	0.150	0.183	0.820	82.8	<b>1</b> 0	0.1416	0.183	0.771	0.799
λ=0.475 μ	83.0	8	0.142	0.183	0.776	89.63	8	0.156	0.183	0.853	83.0	100	0.142	0.183	0.777	0.810
λ=0.500 μ	86.0	100	0.149	0.183	0.805	87.45	8	0.152	0.183	0.830	81.8	8	0.140	0.183	_	0.820
A=0.550 μ	87.9	10	0.153	0.183	0.836	92.90	100	0.164	0.183	0.896	85.0	<b>1</b> 0	0.147	0.183	0.804	0.844
λ=0.589 μ	_	_	_			95.25	100	0.170	0.183	0.930	86.1	97 07	0.150	0.183	0.820	0.868
λ=0.600 μ	89.6	100	0.156	-	0.853	96.50	8	0.171	0.183	0.935	86.2	10	0.150	0.183	0.820	0.873
λ=0.625 μ	93.75	8	0.1655	0.183	0.905	97.75	8	0.174	0.183	0.950	89.3	8	0.1555	0.183	0.850	0.895
$\lambda = 0.650 \mu$	94.0	100	0.1660	0.183	0.907	100.55	901	0.180	0.183	0.985	91.1	100	0.160	0.183	0.875	0.923
λ=0.675 μ	_			_		105.75	8	0.1905	0.183	1.040	•	_				0.950

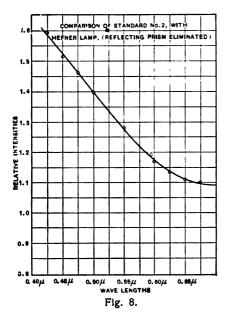
TABLE II.

No. 2.] RADIATION FROM NERNST LAMP.

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illustration, the curve shown in Fig. 7 was obtained in this manner. The readings began in the long waves and extended into the short ones. The potential difference was kept constant but no attention was paid to current strength. The curve obtained is a smooth curve but very different from those obtained later with constant current. On repeating these observations, passing through the spectrum in the reverse order, a curve of quite different shape was obtained. This method, therefore, was evidently unreliable. It is probable that the current strength gradually decreased in value with the time without



giving an apparent change in voltage,<sup>1</sup> thus accidentally giving the curve mentioned. Thereafter, observations were taken with the current kept constant and a series of curves were obtained which were similar to those shown in Fig. 9.

An accident, however, necessitated the remounting of a new glower. The first observations were taken at the rated normal current capacity of the lamp, namely, 0.8 amperes. Observations were then taken with decreasing currents down to 0.2

amperes. Then observations were taken with increasing currents; the maximum value reached was 1.50 amperes, at which point the platinum wire attached to the glower fused off after a few observations had been taken. The mean readings thus taken are recorded in Table III. in the order in which they were taken and are lettered accordingly, beginning  $a, b, c, \ldots$ , etc. The curves obtained from these data are lettered likewise. No stress is laid upon the data obtained in the last set of readings and the curve obtained from these data is given only once — in Fig. 9— after which it is not considered.

<sup>1</sup> This possibility is suggested by a characteristic curve of the glower given by Wurts, Trans. Am. Inst. Elect. Eng., 18, p. 552, 1901.

No. 2.]

## RADIATION FROM NERNST LAMP.

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2	(C) V = 83	V = 83.0; $I = 0.20$ $P = 7.4$ cm.	0 P=7.	4 cm.		<b>*</b>	$(\mathbf{k})$ $V = 78.5$ ; $I = 0.40$ ; $P = 7.4$ cm.	/ = 0.40	: P = 7.	ce.	(i) 	- 87	= / :0	o.80; <i>P</i> =	(i) $V = 87.0$ ; $I = 0.80$ ; $P = 7.4$ cm.
	Dr. Read	Drum Readings Micrometer.	Slit W in n	Slit Widths in mm.	Ratio of Inten-	Dr. Read	Drum Readings Micrometer.	Slit Widthe in mm.	Vidthe am.	Ratio of Inten-	Drum Readings of Microm.	5.6	Slit Widths in mm.	/idths am.	Ratio of Inten-
	S1	S,	S,	s.	-901129	S <sub>1</sub>	s"	S,	s"	silles.	s.	5	S <sub>1</sub>	s"	
	41.1	1000	0.051	2.040	0.0250	68.4	400 0	0.110	0.800	0.1378	73.6	2	0.122	0.120	1.018
	38.8	1000	0.046	2.040	0.0226	73.5	400	0.121	0.800	0.1515	80.2	20	0.136	0.120	1.133
-	40.7	1000	0.050	2.040	0.0245	76.6	400	0.128	0.800	0.1602	90.5	20	0.156	0.120	1.300
	45.1	1000	0.060	2.040	0.0294	91.8	<b>4</b> 00	0.160	0.800	0.2000	113.5	80	0.207	0.141	1.470
						;	00,				(110.7	20	0.202	0.120	1.683)
						2.111	400	0.203	0.800	0.2540	127.0	80	0.240	0.141	1.701
	47.9	1000	0.065	2.040	0.0319	113.0	<b>6</b> 4	0.207	0.800	0.2582	110.6	20	0.201	0.120	1.675
											(112.0	20	0.205	0.120	1.708
											110.8	20	0.203	0.120	1.692
	57.7	1000	0.087	2.040	0.0426	131.8	<b>6</b> 4	0.248	0.800	0.3100	132.4	80	0.252	0.141	1.788
	78.0	1000	0.131	2.040	0.0644	149.6	<b>6</b> 4	0.286	0.800	0.3580					
			_			152.0	400	0.202	0.800	0 3650		-			

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			· • • • • • • • • • • • • • • • • • • •	= 7.4 cm	·		′ = 87.o;	,		
Wave- Lengths,	Drui Readi of Mice	ngs	Slit V in n	/idths nm.	Ratio of Inten-		um lings ometer.		vidths nm.	Ratio of Inten-
	S1	S	S <sub>1</sub>	S <sub>n</sub>	sities.	S,	S <sub>n</sub>	S <sub>1</sub>	S <sub>n</sub>	sities.
λ=0.425 μ	97.2	70	0.174	0.120	1.450	81.0	50	0.137	0.072	1.905
λ=0.450 μ	101.5	70	0.182	0.120	1.517	79.3	50	0.135	0.072	1.877
λ=0.475 μ			1		t	83.6	50	0.144	0.072	2.000
λ=0.500 μ	108.4	70	0.197	0.120	1.642	85.6	50	0.148	0.072	2.060
λ=0.550 µ	128.5	70	0.240	0.120	2.025					I
λ=0.589 μ	1	i i		ł	ł	94.8	50	0.172	0.072	2.385
$\lambda = 0.600 \mu$	134.5	70	0.253	0.120	2.108					
λ=0.625 μ	136.9	70	0.257	0.120	2.140	100.1	50	0.180	0.072	2.500
λ=0.650 μ	149.0	70	0.285	0.120	2.380	104.3	50	0.187	0.072	2.600
λ=0.675 μ	160.3	70	0.310	0.120	2.580	122.0	50	0.226	0.072	3.140
( <i>l</i> ) V	= 86.8 ;	/=1.		7.4 cm.		(m)	V = 87.1	; /=0.8	o; P=7	.4 cm.
λ=0.425 μ	88.6	50	0.155	0.072	2.151	100	76.8	0.179	0.135	1.253
λ=0.450 μ	90.4	50	0.159	0.072	2.210	1				
λ=0.475 μ	91.8	50	0.161	0.072	2.239	100	71.9	0.179	0.124	1.441
λ=0.500 μ	97.3	50	0.173	0.072	2.400	100	69.9	0.179	0.129	1.390
λ=0.550 μ	104.5	50	0.189	0.072	, 2.622	100	63.9	0.179	0.108	1.656
λ=0.589 μ	1					100	60.8	0.179	0.101	1.772
λ=0.600 μ	108.4	50	0.197	0.072	2.740	100	59.6	0.179	0.099	1.810
λ=0.625 μ	109.9	50	0.200	0.072	2.780	100	59.3	0.179	0.097	1.826
λ=0.650 μ	111.1	50	0.203	0.072	2.820	100	56.2	0.179	0.091	1.970
λ=0.675μ	116.5	50	0.215	0.072	2.980		i	1	!	1



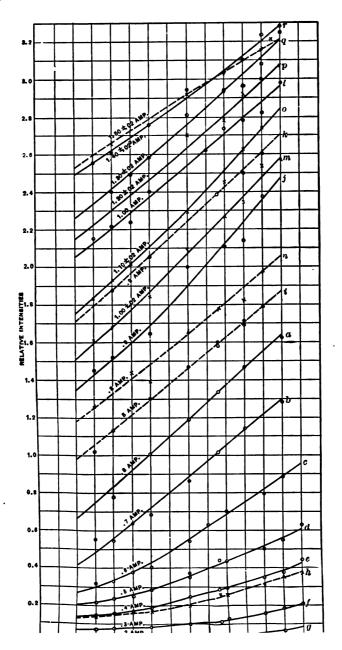
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A (u)	$(n) V = 87.0; J = 1.00 \pm 0.02; P = 7.4 \text{ cm}$	+  8:1 	0.02; P	= 7.4 cm		- A (0)	(o) $V = 87.0$ ; $I = 1.10 \pm 0.02$ ; $F = 7.4$ cm.	11011	0.02; <i>P</i> =	7.4 cm.	A (d)	(b) V = 80.1;	/ = 1.30 ± 0.03;		P = 7.4 cm
Wave- Lengths.	of Micro	Drum Readings Micrometer.	Slit Widths in mm.	/idths mm.	Ratio of Inten-	Drum Readings of Micrometer	Drum Readings Micrometer.	Slit Widths in mm.		Ratio of Inten-	0	Drum Readings f Micrometer.	Slit Widths in mm.	idths Dm.	Ratio of Inten-
	S1	ۍ ۳	S1	s,		S1	·S <sub>n</sub>	S1	s"		S,	S,	S,	S <sup>r</sup>	
λ= 0.425 μ	117.7	80	0.226	0.140	1.613	118.4	70	0.219	0.120	1.828					
$1-0.450 \mu$	126.0	80	0.235	0.140	1.680	123.0	20	0.232	0.120	1.935	500	9 9 4 4	0.394	0.171 0.172	2.300 2.290
λ -0.475 μ	135.6	80	0.255	0.140	1.821	128.8	20	0.241	0.120	2.010	<b>50</b>	92.0	0.394	0.167	2.360
$\lambda = 0.500 \mu$	136.1	80	0.257	0.140	1.835	129.1	20	0.247	0.120	2.060	80	89.6	0.394	0.1595	2.470
λ -0.550 μ	152.3	80	0.293	0.140	2.092	144.8	20	0.275	0.120	2.290	<b>50</b>	82.8	0.394	0.146	2.700
ک⊸0.600 μ	163.9	80	0.317	0.140	2.260	149.3	20	0.280	0.120	2.330	<b>50</b>	80.4	0.394	0.142	2.780
$\lambda = 0.625  \mu$	169.8	80	0.329	0.140	2.344	162.5	20	0.315	0.120	2.620	200	77.6	0.394	0.135	2.920
$\lambda = 0.650 \mu$	183.0	80	0.356	0.140	2.540	170.1	20	0.330	0.120	2.744	<b>50</b>	75.7	0.394	0.131	3.000
λ=0.675 μ	195.2	80	0.384	0.140	2.740	179.6	20	0.350	0.120	2.920	500	60.14	0.394	0.105	3.080
1 (6)	85.05;	$I = 1.30 \pm 0.03$ ; $P = 7.4$ cm	0.03; P	== 7.4 cm	•	(r) V =	- 84.6; /	1.40	1.40±0.02; P		- A (s)	- 84.0; /	- 8.1	84.0; / I.50 ± 0.03; P	- 7.4 cm
λ - 0.425 μ						500	87.4	0.394	0.154	2.560	-				
λ-0.450 μ	<b>50</b>	90.4	0.394	0.164	2.400	500	85.9	0.394	0.151	2.610	<b>5</b> 0	83.3	0.394	0.148	2.660
λ=0.475 μ	<b>50</b>	87.9	0.394	0.158	2.495	<b>5</b> 00	83.9	0.394	0.148	2.661	-				
λ -=0.500 μ	<b>50</b>	85.3	0.394	0.152	2.592	<b>5</b> 00	80.6	0.394	0.143	2.758	<b>5</b> 00	78.5	0.394	0.137	2.880
λ 0.550 μ	500	79.6	0.394	0.140	2.818	<b>50</b>	77.0	0.394	0.134	2.940	200	77.3	0.394	0.135	2.920
λ-0.600 μ	<b>50</b>	76.9	0.394	0.134	2.940	<b>5</b> 0	75.5	0.394	0.130	3.030	200	74.5	0.394	0.130	3.030
λ= -0.625 μ	<b>8</b> 0	76.5	0.394	0.133	2.960	<b>500</b>	74.0	0.394	0.127	3.100		-			
λ= <b>0.650</b> и	80	73.1	0.394	0.128	3.080	500	71.9	0.394	0.122	3.230	<b>500</b>	72.7	0.394	0.125	3.155
λ=0.675 μ	<b>5</b> 00	70.1	0.394	0.121	3.260	200 200	70.0	0.394	0.120	3.280					

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At 1.20 amperes the ballast of the lamp burned out after which the leads to the lamp were connected directly to the terminals of the glower and observations were continued with increasing current strength for each successive set until the maximum was reached. In all about 2,500 observations are represented in the data given in the tables.

In tabulating the data the following symbols are used: P represents the gas pressure in centimeters of water; V, the potential difference in volts between the terminals of the glower;  $S_1$ , the slit width of the collimator for standard No. 1;  $S_2$ , the slit width of the collimator for standard No. 2;  $S_{B}$ , the slit width of the collimator for the Hefner lamp;  $S_n$ , the slit width of the collimator for the order of the order of the order.

At this point it may be noted that the writer is familiar with the work done by Murphy<sup>1</sup> and Capps<sup>2</sup> on the correction for slit widths necessary in spectrophotometric work. No data for this correction with such an instrument as was used here, however, are available. In the second place, correction for slit widths is not so essential here because in the method of using the data given in the tables, the error due to this cause is eliminated, or at least reduced to a minimum. In obtaining the curve showing the relation between the intensities of the Hefner-Altneck lamp and standard No. 1 for waves of different lengths, two curves on different days were carefully determined, and the mean values of the ordinates of these curves were taken and plotted as the ordinates of the curve in Fig. The two curves mentioned are shown in the upper part of Fig. 5. 5 and the data therefor are given in Table I. Thus the intensity in candle power of standard No. 1 for different wave-lengths is determined. The values obtained in the comparison of standard No. I with standard No. 2 were treated in a similar manner and the curve, as shown in Fig. 6, obtained. If now the values of the ordinates of the curve in Fig. 6 be multiplied by the corresponding ordinates of the curve in Fig. 5, and if these new values thus obtained be plotted as ordinates with the corresponding wave-lengths as abscissæ, the curve shown in Fig. 8 will be obtained. This

> <sup>1</sup> Murphy, Astrophys. Jour., 6, 1, 1897. <sup>2</sup> Capps, Ibid., 11, 25, 1900.

curve shows the relation existing between the intensity of the acetylene flame used as a standard unit of comparison and the intensity of the Hefner lamp when the influence of the totally reflecting prism is eliminated. This curve agrees with results previously obtained.<sup>1</sup> It is to be noted here that the Hefner lamp was 10 cm. from the collimator slit while the acetylene standard No. 2 was 50 cm. from the slits. Their relative positions are indicated in Fig. 4.

If the values of the ratios of intensities given in Table III, are plotted as ordinates and corresponding wave-lengths as abscissæ, the curves shown in Fig. 9 are obtained. If the ordinates of these curves are divided by one fourth of the corresponding ordinates of Fig. 6 and the values thus obtained are plotted as ordinates with wave-lengths as abscissæ, a series of curves will be obtained showing the relation between the intensities of the Nernst lamp glower at different current strengths and standard No. 2, when both are at a distance of 100 cm. from the collimator slits. These curves are shown in Fig. 10. In these curves the absorption of the totally reflecting prism has been eliminated and the error due to slit widths reduced to a minimum. From an inspection of these curves it is obvious that until a current strength of one ampere is reached the increase in intensity of the glower as compared with acetylene is more rapid in the long waves and less rapid in the short ones. Above this value of the current, the increase in intensity in the region of the short waves is more rapid and there is an apparent decrease in intensity in the region of the long waves beyond 0.600  $\mu$ .

If the ordinates of the curve in Fig. 9 be multiplied by the corresponding ordinates of the curve in Fig. 5 and if the values thus obtained be plotted as ordinates with corresponding wave-lengths as abscissæ, the curves shown in Fig. 11 will be obtained. These curves show the relation, wave-length by wave-length, between the relative intensities of the Hefner lamp when it is placed 10 cm. in front of the collimator slits and the Nernst lamp when the latter is placed 100 cm. in front of the slits. These curves confirm the conclusion deduced from the curves in Fig. 10, showing that with a current above 0.90 or 1.00 ampere there is a marked increase in

<sup>1</sup> Hartman, PHYS. REV., 9, p. 185, 1899.

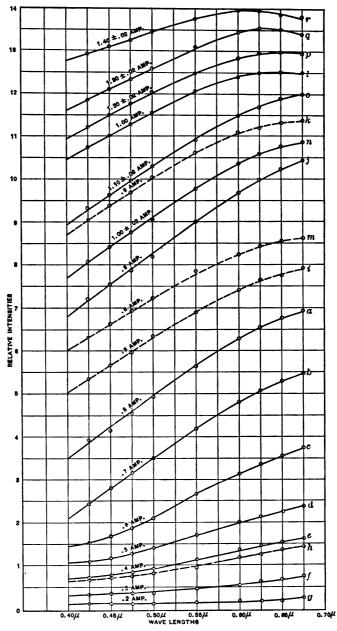
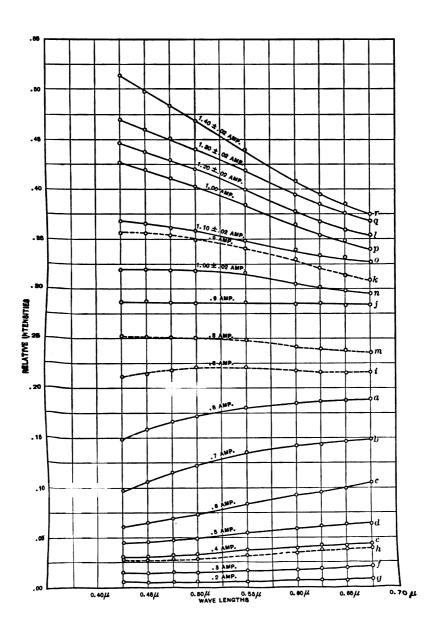


Fig. 10. Comparison of the Nernst lamp at various current densities with standard No. 2. The curves are corrected for absorption and slit widths. Intensities compared with both sources 50 cm. from the collimator slit.

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intensity in the region of the short waves and a corresponding decrease in the intensity of the long waves. Below this value of the current the opposite is true, the increase in intensity being most rapid in the long waves.

It will be noted that a number of the curves are drawn in dotted lines and that these dotted curves bear the same values of current strength as some one of the full line curves beneath them. To this statement there is but one exception, in which case the difference is so small that it may reasonably be ascribed to errors in observation. In the other cases this explanation will not suffice. It will be noted, however, that these dotted curves were obtained at a date later than that on which the full line curves of the same current strength were obtained. Apparently, therefore, this indicates an increase in the intensity of the light emitted from the glower as it ages, even though the current be kept constant. One would expect this if the glower gradually wastes away with continued use and thus decreases in cross-section, for under these conditions a given current would make the glower corresponding hotter the smaller it becomes. There is. however, a probable limitation to this.

In the case of the curves in which the current was furnished by the department alternator, the disturbing factors were under such complete control that the current was kept practically constant. The maximum voltage of the alternator, however, could not be raised to a value high enough to send through the glower a current above 1.00 ampere. After this value was reached, the city 208-volt A. C. mains were used. The conditions were now more unsteady and the needle of the ammeter vibrated through a range of 0.04 'amperes and the current values are so indicated. Thus  $1.00 \pm 0.02$ amp. means that the current fluctuated between 0.98 and 1.02 amperes. The reason for the decrease in intensity when current taken from this source was used is not evident to the writer; in both cases current was furnished by a 60-cycle machine.

It will be interesting to compare the luminous radiation from the glower of the Nernst lamp with the radiation from a number of

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spectrum is arbitrarily taken as unity. In the other sources considered that portion of the spectrum in the region of the D line is taken as unity. Plotting wave-lengths as abscissæ and relative intensities as ordinates the series of curves shown in Fig. 12 is ob-

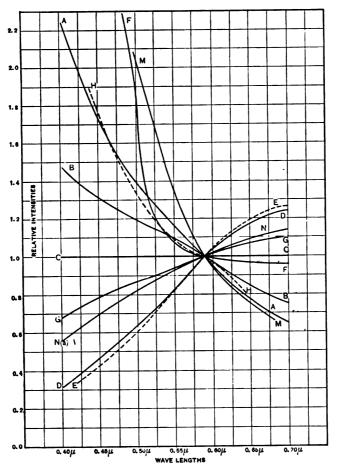


Fig. 12. Color of (A) acetylene in oxygen, (B) acetylene-hydrogen in oxygen, (C) acetylene in air, (D) kerosene lamp, (E) ordinary gas flame, (F) fresh lime light, (G) old lime light, (H) arc light, (M) magnesium light and  $(N_a)$  Nernst lamp. Standard, an acetylene flame.

tained. It will be observed that the curve for the Nernst lamp glower, which was taken for the rated normal current strength of 0.80 ampere corresponds most nearly to the radiation from old lime. The data for many of these curves have been taken from a paper by Professor E. L. Nichols.<sup>1</sup>

In order to have a basis from which to start, it has been arbitrarily assumed in Fig. 13 that the values given by Abney for the luminosity curve of the normal eye<sup>2</sup> would give the luminosity curve of the acetylene flame. The luminosity curves of the Nernst

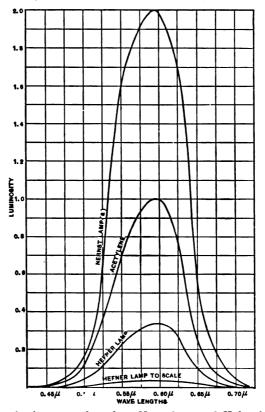


Fig. 13. Luminosity curves of acetylene, Nernst lamp, and Hefner lamp. Abney's normal luminosity curve assumed for acetylene.

lamp and the Hefner lamp were then plotted on the same sheet with this curve. The luminosity of the spectrum of acetylene is taken as unity in the region of the D line. In this figure the Nernst lamp curve is reduced to one third its actual size and the curve of the Hefner lamp is magnified ten times. The lower curve repre-

> <sup>1</sup>Nichols, Jour. Frank. Inst., 150, p. 356, 1900. <sup>2</sup>Abney, Color Vision, p. 211, 1895.



sents the actual luminosity curve of the latter as compared with the acetylene standard No. 2. The luminosity of the Nernst lamp is therefore much greater than that of the acetylene flame.

Since preparing the above, through the courtesy of Dr. Frank Allen, of Cornell University, a luminosity curve of the acetylene flame has been obtained. The luminosity curves of the Nernst and Hefner lamps as compared with acetylene, using this luminosity curve as a basis, are plotted, as described above, in Fig. 14.

To summarize, it appears that at the rated normal current strength the radiation from the glower of the Nernst lamp is relatively rich in the more luminous waves of the spectrum; it exhibits no marked

selective radiation; its light intensity apparently increases with age; its light is relatively less rich in the short, but richer in the long waves than that from the acetylene flame, but its radiation rapidly becomes more like that from burning acetylene with increasing current strength; at current strength below the rated normal value, the increase in intensity with increasing current strength is most marked in the long waves, and above this rated normal value of current strength the increase in intensity is most rapid in the short waves; at current strengths below the rated nor-

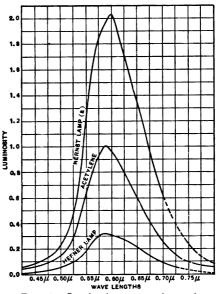


Fig. 14. Luminosity curves of acetylene, Nernst lamp, and Hefner lamp. Luminosity of the acetylene flame based on Allen's curve.

mal value the Nernst lamp is relatively less rich in short waves than the flame of the Hefner lamp, while above this current strength the

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The apparatus used in this investigation has been generously placed at my disposal by Professor Arthur W. Goodspeed, of the Department of Physics, and it is with a sense of gratitude and pleasure that I acknowledge all that he has done to satisfy my every need and thus make this investigation a success. In conclusion, therefore, I take pleasure in thanking him, as well as Dr. Horace C. Richards, for the suggestions they have made and the courtesies they have shown in the course of this investigation.

Randal Morgan Laboratory of Physics, University of Pennsylvania, April 10, 1903.

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## THE PRESSURE DUE TO RADIATION.<sup>1</sup>

#### (SECOND PAPER.)

#### BY E. F. NICHOLS AND G. F. HULL.

"HE disc was calibrated for temperature in terms of the deflection for a definite sensitiveness of the galvanometer  $G_1$ . For this purpose the disc was immersed in a kerosene bath and the galvanometer deflection measured for two different temperatures of the disc. One of these was about 18° C. above the comparatively steady temperature of the room, or calorimeter containing the standard temperature junctions (see Fig. 6), and the other about the same number of degrees below the room temperature. These two temperatures were measured by a Fuess standard thermometer divided into tenths of a degree and calibrated at the Reichsanstalt. Two calibrations of the silver disc were made some days apart. One of these series appears in full in Table V. The first three columns of the table give the zero, direct and reversed reading of the galvanometer  $G_1$ . The fourth column gives the temperature of the bath in which the disc was immersed, and the fifth, that of the constant temperature calorimeter. The sixth column gives the deflections of  $G_1$ . The seventh column the means of the alternate deflections. The eighth, the mean of the two columns preceding it. The last column gives the difference in temperature between the two calorimeters in degrees C. For the total temperature range in the table, 39.11°, the deflection of  $G_1$  was 393.8 scale divisions for a sensitiveness of  $G_1 = 996$ . A range of one degree would thus give a deflection of 10.03 divisions for a sensitiveness of  $G_1 = 1,000$ . The mean of two separate calibrations was 9.96 scale divisions for one degree temperature difference.

Defers having a series of intensity massivements the disc use

## TABLE V.

Cali	bratio <b>n</b>	of	Silver	Disc.

\_\_\_\_\_

			Co	old Bath.				
	G <sub>1</sub> Reading	1	Disc $T_1^{\circ}$	Room cal. T.º	Deflection of $G_1$	Means of Alter- nate Deflec-	G <sub>1</sub> Means.	T,°T,
Rev.	Zero.	Direct.		•	0. 01	tions.		
	221.2							
	221.0	35.2	1°.58	20°.05	185.8	h	]	
	220.9							
402.0	221.0		1°.60	20°.07	ן 181.0	}185.7	183.4	18.47
	221.2							
	221.2	35.7	1°.57	<b>20°</b> .10	185.5	J 181.3	183.4	18.53
402.1	221.2		10 50	000.14	101 (	, 107 0	102 8	10 70
403.1	<b>221.5</b> 221.9		1°.56	20°.14	181.6 <sup>J</sup>	185.8	183.7	18.58
	221.9 222.0	35.9	1°.54	20°.16	186.1	182.2	184.1	18.62
	222.1	55.9	1.34	20.10	100.1	104.4	101.1	10.02
405.0	222.2		1°.52	20°.20	182.8	186.3	184.5	18.68
	222.4							
	922.7	36.2	1°.57	20°.22	186.5	182.7	184.6	18.65
	223.0					11		
405.8	228.1		1°.60	20°.26	182.7	<b>}186.7</b>	184.7	18.66
	223.2							
	223.8	36.3	1°.59	20°.30	187.0	נן		
	223.5					l	184.0	18°.60
	Correc	tion to $T_1$						
			<b>`</b>	Varm Bat	:h.			
	217.3	434.2	41°.45	000 40	015 6	1		
	<b>218.6</b> 219.9	434.4	41°.45	20°.40	215.6	]		
2.0	219.9 220.5		41°.35	20°.42	218.5	213.7	216.1	20.93
2.0	221.1		12 .05	20.42	210.5			20.75
	222.4	434.2	41°.25	20°.44	211.8	216.4	214.1	20.81
	223.7							
10.0	224.4		41°.08	20°.50	214.4	209.1	211.7	20.58
	225.1		I.			ļ	ŀ	
	225.7	432.1	40°.90	20°.55	206.4	212.4	209.4	20.35
	226.3		1					i I
16.3	226.7		40°.80	20°.60	210.4	204.8	207.6	20.20
	227.2							
	<b>227.8</b>	431.0	40°.67	20°.61	203.2	208.5	205.8	20.07
21.8	228.4 228.5		40°.55	20°.63	206.7	201.8	204.2	19.92
<i>4</i> 1.0	228.7 228.7		+0*.55	<i>4</i> 0°.03	200.7	201.0	£04.2	17.94
	228.7 229.0	429.4	40°.43	20°.65	200.4	J	209.8	20°.41
	229.3	12017	10 110		2001 T			
		tion to $T_1$	'					

·



surrounded by a jacket of ice and salt. The disc was thus lowered to a temperature of about zero degrees and was then quickly transferred to the chamber C (Fig. 6), and the beam was directed upon it. When its temperature had risen to within five or six degrees of that of the chamber C, galvanometer readings were made at intervals of five seconds until the disc was heated to a temperature several degrees above its surroundings. The temperature of the chamber C was determined by removing the disc and cooling it to a point near the room temperature, then replacing it and observing its rate of temperature change for several minutes.

The note-book record of one series of observations showing the heating of the disc by the light beam is given in full in Table VI. It will be seen from the table that the temperature of the disc passed

Table	VI.
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August 16. Energy Measurements. Through Air. Series 4. Zero of Galvanometer  $G_1$  (closed circuit) Determined by Method of Cooling = 216.8 = Reading at Room Temperature.

Time.	G,	Time.	G,	∆G <sub>1</sub>	$\Delta t \qquad \frac{\Delta G_1}{\Delta t}$	
0 secs.	174.5	60 secs.	253.2	78.7	60 secs.	1.312
5 "	182.0	55 "	247.3	65.3	50 "	1.306
10 "	189.0	50 "	241.3	52.3	40 "	1.308
15 "	<b>196.2</b>	45 "	235.2	39.0	30 ''	1.300
20 ''	203.0	40 "	229.1	26.1	20 **	1.305
25 ''	209.7	35 ''	222.8	13.1	10 "	1.310
30 "	216.4	1			Average	1.307

The lamp reading  $(G_1)$  was 924.

The sensitiveness of  $G_2$  was 667, and of  $G_1$  was 996.

 $\frac{\Delta G_1}{\Delta G_1}$  reduced to standard conditions becomes

 $1.307 \times 667 \times 996 \div (924 \times 1,000) = 0.943$  mm. per sec.

that of the chamber thirty seconds after the beginning of the series. The readings of  $G_1$  at equal time intervals on either side of the zero are on horizontal lines. The last column of the table contains the rate at which the galvanometer deflection was changing when the disc and its surroundings were at the same temperature.

Energy series were made "through air," "through red glass," and "through water cell," as in the pressure measurements. During the experiment the black coatings were frequently cleaned off from the disc and new ones deposited. The final result therefore does not correspond to an individual, but to an average coating.

To correct for any inequality between the two disc thermo-junctions or any lack of symmetry in their positions, referred to the central plane of the disc, which might prevent the mean temperature of the two junctions from representing the mean temperature of the mass, series of observations were made on each face of the disc. The

		Thre	ough A	ir.		Throu	gh R	ed Glass.	Throu	gh W	ater Cell
Date.	8 <i>G</i> 1 8 <i>t</i>	(Lamp).	<i>S</i> 1	5g	$\begin{cases} \delta G_1 \\ \delta t \\ \text{Reduced} \\ \text{to} \\ \text{Standard} \end{cases}$	$\frac{\delta G_1}{\delta t}$	G,	$\frac{\frac{\delta G_1}{\delta t}}{\operatorname{Reduced}}$ Standard	8G1 81	G,	δG1 δ/ Reduced to Standard
Aug. 10	1.387	980	990	689	.965		1		.437	345	.864
• ••	1.263	920	990	689	.936				.400	311	.877
** **		1							.369	279	.902
" 11	1.244	866	986	701	.992	.750	546	.950	.412	315	.905
** **	1.455	1010	986	701	.995	.750	546	.950	.510	382	.922
** **	1.505	1047	986	701	.994			1	.516	381	.935
" 16	1.447	1022	996	669	.942	.736	529	.927	.416	327	.873
** **	1.284	886	996	669	.966	.740	,527	.936	.451	352	.853
** **	1.316	925	996	669	.948	.797	550	.965	.502	382	.875
** **	1.307	924	996	669	.943						
·· 18	1.598	1110	995	667	.955	.738	515	.952	.449	333	.895
** **	1.550	1047	995	667	.984	.732	518	.940	.445	342	.865
** **	1.548	1031	995	667	.995	.730	518	.938	.451	346	.867
** ** ,	1.410	957	<b>9</b> 95	667	.977		i i				
	1.330	898	995	667	.983					1	
. 19	1.241	862	1001	675	.975	.760	532	.965	.451	343	.892
	1.360	934	1001	675	.985	.728	512	.960	.452	338	.904
** **	1.324	905	1001	675	.990	.738	525	.950	.466	351	.898
	1.364	934	1001	675	.988			l,			
	• •	1	Averag	e	0.973	Ave	rage	0.948	Ave	rage	0.888
				-1	- 0.003		E	-0.002		=	- 0.004

Table	V	II.
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Front	Face.
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black coating was always cleaned off from the face of the disc away from the light. All of the series of energy measurements are gathered together in Tables VII. and VIII. In the tables, under the head "through air," the first column contains the observed rate of increase in the galvanometer deflection  $G_1$ , when the disc and its surroundings were at the same temperature; the second column,

		Through Air.					Thre	ough I	Red Glass.	Through Water Cell.		
Date.		8 <i>G</i> 1 8 <i>t</i>	Gs (Lamp).	<i>S</i> 1	S2	$\frac{\delta G_1}{\delta t}$ Reduced to Standard.	$\frac{\delta G_1}{\delta t}$	G,	$\frac{\delta G_1}{\delta t}$ Reduced to Standard.	8G1 8t	G,	$\begin{cases} \delta G_1 \\ \delta t \\ Reduced \\ to \\ Standard \end{cases}$
Aug.	12.	1.374	960	991	684	.970	.808	578	.949	.495	370	.906
"	12.	1.331	932	991	684	.968	.740	536	.935	.434	320	.919
**	12.	1.284	900	991	684	.967	.765	542	.957	.489	371	.895
"	15.	1.428	992	996	670	.960	.703	506	.926	.490	368	.890
**	15.	1.428	984	996	670	.968	.742	526	.941	.466	352	.885
**	15.	1.531	1068	996	670	.962	.765	551	.926	. <b>440</b> <sup>′</sup>	337	.873
**	20.	1.477	1047	996	685	.961	.703	522	.918	.458	375	.833
**	20.	1.520	1090	996	685	.951	.760 <sup>1</sup>	537	.965	.497	400	.848
**	20.	1.576	1130	996	685	.951	.781	570	.935	.507	408	.848
" "	20.	1.568	1124	996	685	.950				į '		
"	21.	1.783	1224	995	668	.970	.846	604	.932	.503	<b>393</b>	.852
"	21.	1.773	1232	995	668	.957	.790	575	.915	.481	377	.850
"	21.	1.705	1190	995	668	.953	.803	575	.930	.483	373	.862
"	21.	1.452	1019	995	668	.948				i		
	Average			0.960	Average		0.936	Average 0.872				
					Ŧ	- 0.0014	1		$\pm 0.003$		±	0.005

#### TABLE VIII.

Rear Face.

the corresponding mean lamp deflections of galvanometer  $G_2$ . The third and fourth columns contain the sensitiveness of galvanometers  $G_1$  and  $G_2$ , respectively, and the last column the values of the first column reduced to standard lamp and standard sensitiveness of both instruments. The series on the two faces of the disc are recorded and averaged separately, then combined with their probable errors in the general average at the end of Table VIII.

Tables VII. and VIII. give the following results: The average increase in the reading of  $G_1$  for standard conditions is 0.966 mm. per second. From the thermal calibration, a deflection of 9.96 divisions corresponds to a temperature difference of 1° C. Consequently the rise in temperature of the silver disc per second when the light passed:

(a) through air =  $0.966 \div 9.96 = (0^{\circ}.0970 \pm 0^{\circ}.00034 \text{ C.}).$ 

(b) through red glass =  $0.942 \div 9.96 = (0^{\circ}.0946 \pm 0^{\circ}.00036 \text{ C}.)$ .

(c) through water cell =  $0.880 \div 9.96 = (0^{\circ}.0884 \pm 0^{\circ}.00064 \text{ C.}).$ 

The mass of the silver disc was 4.80 grams, its specific heat<sup>1</sup> at  $18^{\circ}$ C. = 0.0556; the mechanical equivalent of heat at  $18^{\circ}$  C. = 4.272  $\times 10^{7}$  ergs.<sup>2</sup> Consequently the energy of the standard radiation is

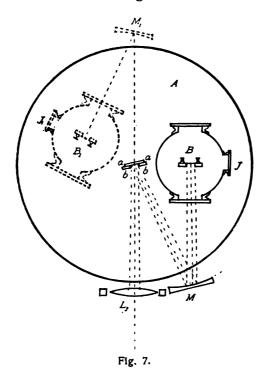
- (a) through air,  $0.0970 \times 4.80 \times 0.0556 \times 4.272 \times 10^7$ or  $E_a = (1.108 \pm 0.004) \times 10^6$  ergs per second.
- (b) through red glass,  $E_g = (1.078 \pm 0.004) \times 10^6$  """""
- (c) through water cell,  $E_{w} = (1.008 \pm 0.007) \times 10^{6}$  """""

Reflecting Power of the Surfaces Used.

According to Maxwell and Bartoli, the pressure in dynes per square centimeter for normal incidence is equal to the energy in ergs in unit volume of the medium. The energy in unit volume is made up of both the direct and reflected beams. If E is the intensity of the incident beam and  $\rho$  the reflection coefficient, the pressure  $p = \frac{E(1 + \rho)}{V}$ , where V is the velocity of light. The methods for measuring b and E have already been described. The determination of  $\rho$  for both sides of the vanes C and D was made as follows. The supports of the torsion balance were replaced by the divided circular plate A (Fig. 7), of a force table which could be rotated about a central, vertical axis. The rod about which the plate turned passed up through the plate and at its top the mirror holder bb was fastened. The vanes were freshly silvered and mounted on a plate glass carrier *aa*, which was held by a clamp against the back face of bb. The beam was directed on the vanes by the lens  $L_{3}$  (Figs. 3 and 7) exactly as it had been in the pressure observations. After reflection from the vane the beam fell on a concave mirror M which projected an image of the vane upon a simple sheet bolometer B, forming the unknown resistance of a post-officebox bridge. The current was supplied from storage cells and the

bell-jar used earlier. The mirror M, the bell-jar and bolometer were attached to the plate of the force table. The full line diagram shows the arrangement for reflection. The dotted figure shows the position for a measurement of the direct beam. All measurements of direct reflection were made for an angle of incidence of  $12^{\circ}$ .5.

The method of observing will be seen from the note-book record of a single series of measurements given in Table IX. In the table,



D and R indicate direct and reflected beams, respectively. The first and second columns contain the zero points and end of swings of the galvanometer  $G_1$ , and the third column, the deflection. The remaining columns, in order, contain the lamp galvanometer deflection; the deflection of  $G_1$  reduced to constant lamp; the means of each pair of D or R values; the means of alternate readings; and the final column, the quotients of the two preceding columns which are the reflection coefficients sought. In all, three series of measurements were made on the silver, and two series on the glass-silver

G	ı	Deflect	·	<i>G</i> ,		Alternate	Reflection	
Zero. Turning Point.		G <sub>1</sub>	Lamp.	Reduced to Standard.	Averages.	Averages.		
R 350.0	159.5	190.5	132.6	143.8	1			
349.0	152.0	197.0	139.3	141.3	<b>142.5</b>			
D 349.5	100.5	249.0	136.8	182.1	5			
350.0	111.5	238.5	130.5	183.0	<b>182.5</b>	142.0	.779	
R 346.0	177.0	169.0	119.3	141.2	5			
347.0	171.0	176.0	124.4	141.7	<b>} 141.5</b>	182.5	.775	
D 348.5	123.0	225.5	124.0	181.8	182.4	1	-	
348.5	120.0	228.5	125.0	183.0		J 141.1	.773	
R 345.0	172.0	173.0	122.6	141.0	} 140.6 J			
345.0	171.0	174.0	124.0	140.3		182.7	.770	
D 346.0	132.0	214.0	115.5?		1			
346.0	124.0	221.0	120.7	183.0	} 183.0	141.2	.773	
R 344.0	173.0	171.0	120.7	141.8	} 141.7			
344.5	171.0	173.5	122.6	141.6		182.1	.778	
D 346.0	119.0	227.0	125.3	181.0	} 181.2		-	
346.0	117.5	228.5	126.0	181.3		141.6	.781	
R 342.0	174.0	168.0	118.0	142.3	1			
342.0	170.5	171.5	122.0	140.8	} 141.5	181.8	.780	
D 347.0	130.0	217.0	119.0	182.3	} 182.5		-	
347.0	134.0	213.0	116.7	182.7		141.4	.775	
R 341.5	174.5	167.0	118.0	141.3	1			
341.0	173.0	168.0	119.0	141.1	} 141.2			
				•	i	Average	0.776	

TABLE IX.

October 31, 1902. Reflection Coefficient of Dg. Air.

faces of each vane. To get average coefficients which would represent the range of condition of the mirrors during the pressure measurements, the vanes were cleaned and new silver coatings deposited between each two series on the same vane. The reflection coefficients are collected in Table X. For each surface studied the diffused reflection for a beam which had traversed air was determined by setting the mirror holder for normal incidence. The diffuse energy reflected at an angle of 25° falling on the full aperture of the mirror M was measured, and the total diffuse energy for the hemisphere computed on the basis of the cosine law. If  $I_{\theta}\partial A$  is the amount of diffuse radiation falling normally upon the area  $\partial A$ , distant r from the vane and at an angle  $\theta$  with the incident radiation, then  $I_{\theta}\partial A = I_0 \cos \theta$   $\partial A$ . The total amount of diffuse radiation  $= \int \int I_0 \cos \theta \partial A$ ,

#### No. 2.] THE PRESSURE DUE TO RADIATION.

over the surface of the hemisphere  $= \int_0^{\frac{\pi}{2}} 2\pi r^2 I_0 \cos \theta \sin \theta \partial \theta$  $= \pi I_0 r^2$ . This integral is the amount of the diffuse radiation in Table X. The force, due to radiation of intensity  $I_0 \partial A$ , normal to the vein is  $I_0 \cos \theta \partial A$ , and the total is equal to  $\int_0^{\frac{\pi}{2}} 2\pi r^2 I_0 \cos^2 \theta \sin \theta$  $\partial \theta = \frac{2}{3} \pi I_0^2$ . It is thus seen that of the diffuse reflection, two

#### TABLE X.

		С.				(	<b>.</b>	
	Through Air.	Red Glass.	Water.	Diffuse.	Through Air.	Red Glass.	Water.	Diffuse
	92.8	94.5	88.9	0.98	77.8	75.9	80.8	
	89.8	90.8	86.0	0.92	77.6	76.6	80.0	1.6
	90.8			1.23				
Average	91.1	92.7	87.5	1.04	77.7	76.3	80.4	1.6
		D				1	P	
	95.0	96.3	91.5	2.2	77.6	76.5	81.0	2.8
	92.0	94.0	90.4		76.7	75.2	79.7	2.2
	94.8	95.0	92.3	0.8				
Average	93.9	95.1	91.4	1.5	77.2	75.9	80.4	2.5

#### Reflection Coefficients in Percentages.

Average Reflection	
--------------------	--

A	ir-Silver.			Ì	Glass-S	Bilver.	
92.5	93.9	89.5	1.3	77.5	76.1	80.4	2.0
	Cor	rected R	flection (	Coefficients.			
02.0	93.4	89.0		77.6	76.2	80.5	

thirds is effective as light pressure. This increases the air-silver reflection coefficients by 0.9 per cent. and the glass-silver values by 1.3 per cent. The small glass rod d (Fig. 2), not present in the reflection measurements, decreased the reflecting area of the silvered surfaces in the pressure measurements by 1.54 per cent. The air-silver values are thus decreased by  $0.92 \times 1.54 = 1.4$  per cent., and the glass-silver values by  $0.78 \times 1.54 = 1.2$  per cent. The application of these two corrections gives the final corrected coefficients

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in Table X. The diffuse reflection of black coatings deposited by the method used in blackening the silver disc was measured and computed in the same manner as the diffused reflection from the vanes C and D. The agreement found by Angström<sup>1</sup> between the diffuse reflection of matte surfaces for normal incidence, and the cosine law was abundantly close for the present purpose. Five determinations of this reflection were made under different conditions and with different coatings. The values in percentages of the incident beam were 4.4 per cent., 4.5 per cent., 4.2 per cent., 4.6 per cent. and 5.2 per cent.; average, 4.6 per cent. Thus only 95.4 per cent. of the incident beam was absorbed by the black coating on the silver disc in producing the temperature increase observed. Hence the true energy of the beam is equal to the observed energy divided by 0.954.

The silver disc, diameter 13.3 mm., used in the energy measurements, received long waves and scattered radiation which passed round and through the light pressure vanes of diameter 12.8 mm. This amount was experimentally determined for both thin and thick silver coatings in order to approximate to the average condition of the coatings in the light pressure measurements and it was found to average (a) through air, 1.40 per cent.; (b) through red glass, 1.44 per cent.; (c) through water, 0.46 per cent. On this account the energy E of the standard radiation must be reduced by the above. percentages.<sup>2</sup> Applying these corrections and the corrections due to the diffused radiation from the black coating on the silver disc, the energy of the standard radiation becomes

(a) through air,  $E_a \times \frac{0.986}{0.954}$ ; (b) through red glass,  $E_g \times \frac{0.986}{0.954}$ ; (c) through water,  $E_w \times \frac{0.995}{0.954}$ . <sup>1</sup> K. Ångström, Wied. Ann., XXVI., 271, 1885.

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Hence the pressure produced by standard radiation calculated by Maxwell's formula,

$$p = \frac{E(1+\rho)}{3 \times 10^{10}},$$

since  $\rho = 0.848$ , becomes

(a) through air 
$$p_a = E_a \times \frac{1.848}{3 \times 10^{10}} \times \frac{0.986}{0.954}$$
  
=  $1.108 \times \frac{1.848}{3 \times 10^{10}} \times \frac{0.986}{0.954} \times 10^6$  dynes  
=  $(7.05 \pm 0.03) \times 10^{-5}$  dynes;  
(b) through red glass  $p_g = E_g \times \frac{1.848}{3 \times 10^{10}} \times \frac{0.986}{0.954}$   
=  $1.078 \times \frac{1.848}{3 \times 10^{10}} \times \frac{0.986}{0.954} \times 10^6$  dynes  
=  $(6.86 \pm 0.03) \times 10^{-5}$  dynes;  
(c) through water  $p_a = E_a \times \frac{1.848}{3 \times 10^{10}} \times \frac{0.995}{0.954}$   
=  $1.008 \times \frac{1.848}{3 \times 10^{10}} \times \frac{0.995}{0.954} \times 10^6$  dynes  
=  $(6.48 \pm 0.04) \times 10^{-5}$  dynes.

A comparison of observed and computed pressures follows :

	Observed Values in 10 <sup>-4</sup> Dynes.	Computed Values in 10-8 Dynes	Obs. — comp. in Percentages.
Through air,	$p_a = 7.01 \pm 0.02^1$	$7.05 \pm 0.03$	-0.6
Through red glass,	$p_g = 6.94 \pm 0.02$	$6.86 \pm 0.03$	+ 1.1
Through water,	$p_{\rm w} = 6.52 \pm 0.03$	$6.48 \pm 0.04$	— <b>0.6</b>

<sup>1</sup> The pressure and energy measurements for the three different wave groups through air, red glass and water cell constitute three independent experiments. In the values for pressure, 7.01, 6.94, 6.52, equality is not to be looked for. The difference arises from the different reflecting power of the  $45^{\circ}$  glass plate (Fig. 3) for the different beams and from the fact that the indications of the lamp galvanometer  $G_s$  connected with the bolometer R, were probably not strictly proportional to energy for throws differing as widely as 33, 60 and 100, which, roughly, were the relative intensities of the beams through water cell, red glass and air. The function of the lamp bolometer and galvanometer was purely to keep a check on the small variations of the lamp which rarely fluctuated more than 10 per cent. on either side of the mean value. An estimate of the approximate magnitude of the gas action not eliminated by the ballistic method of observation, may be reached from the following considerations.

When radiation falls upon a vane of the torsion balance, part of it is absorbed by the silver surface. From the amounts directly and diffusely reflected, as given in Table X., the amount transmitted by the average surface (experimentally determined but not given in Table X.), the effect of the glass rod and the reflection coefficient of the glass surface, it was found that, when the silver side of the vane was toward the radiation source, the absorption coefficient for radiation through air was 6 per cent. and when the glass surface was forward, it was 18 per cent.

The total force acting on the vane is made up of two parts, that due to radiation pressure and that due to gas action. Let  $F_r$  be the force due to the first cause, assuming that all the radiation is absorbed, and  $F_g$  the effect due to the second, on the same condition. Then the total effect, when the silver side of the vane is forward and the radiation is "through air," is  $1.92 F_r + 0.06 F_g$ . When the glass side is forward the total effect is  $1.776 F_r - 0.18$  $F_g$ . Making these expressions equal to the reduced deflection (Table III., columns 11 and 12) on the silver and glass surfaces respectively, we have two equations by means of which the values of  $F_r$  and  $F_g$  may be obtained. Hence the effect due to gas action on each face of the vane is approximately determinate, as is also the part  $(0.06F_g)$  not eliminated when we average the two columns to obtain column 13.

Applying this method to all the results of Table III. (with the exception of those results taken with poor mirrors as shown by our notes), the gas action present in the ballastic deflections "through air" is 0.8 per cent. Applying the corresponding data and equations to Table IV., the gas action present in the red glass values is I.I per cent. and in the water cell values, 0.3 per cent. The sign of  $F_g$  comes out negative, which means that the gas action was suction.

This reasoning assumes that the glass faces of the vanes during the six seconds' exposure are not warmed by absorption nor by the conduction of heat through the thin glass from the silver coating. The effect of any such absorption or conduction would be to diminish the computed gas action. As estimated from the static observations, the gas action in the ballistic measurements is comparable in magnitude with the computed values obtained above, and of the same sign. Both results show that the uneliminated gas action by the most liberal estimate cannot have exceeded one per cent. of the radiation pressure. Because of its smallness and indefiniteness no correction for gas action has been made to the final pressure values. If corrections were applied its effect would be to slightly reduce the observed pressures.

Aside from the measurements of pressure and energy for which the probable errors are given, the percentage accuracies in the other measurements entering into the computations, and their effects upon the final result follow :

#### 1. Quantities which affect individual series :

(a) Pressure values —

			Per cent	t.	Pe	r cent.
Period of balance,	Τ,	accurate	to 0.2;	effect on	result	0.0
Lever arm of balance,	l,	**	0.1;	**	**	0.0
Constant of galvanometer	G.,		0.5;	**	"	0.0
Estimate of possible error	due	:				
to changing ratio of pe	riod	l				
of $G_2$ to length of expo	sure	:				
of bolometer,		"	0.4;	"	"	0.1

(b) Energy values ----

Constant of	galvanometer	G <sub>1</sub> ,	accurate	to <b>0.1</b> ;	effect of	on result	0.0
66	**	G,,	**	0.5;	* *	"	0.0

- 2. Quantities which affect final averages :
  - (a) Pressure values —

		Per cer	it.	Per	cent.
Torsion of fiber,	accurate	to 0.2;	effect on	result	0.2
Reducing factor 1.357,	**	0.1;	"	"	0.1
Reducing factor 1.550 for $G_2$ ,	44	0.2;	"	"	0.2
Reflection of surfaces of vane	:5, ''	0.4;	"	"	0.2

(A) Fremerou values

From the agreement, within the probable error, of the air, red glass and water values with the theory, it appears that the radiation pressure depends only upon the intensity of the radiation and is independent of the wave-length.

The Maxwell-Bartoli theory is thus quantitatively confirmed within the probable errors of observation.

To Professor J. L. Mann and Messrs. J. A. Brown, Philip Fox, L. E. Woodman, H. R. Willard, H. E. K. Ruppel, and A. V. Ruggles, the writers are indebted for friendly assistance given at some of the stages in the protracted course of these experiments.

WILDER LABORATORY, DARTMOUTH COLLEGE, HANOVER, N. H., February, 1903.



### THE SPECIFIC HEAT OF SOLUTIONS. IV.

#### BY WILLIAM FRANCIS MAGIE.

I. This paper is a continuation of others published under the same title in this REVIEW, Vols. IX., XIII., XIV. It presents the specific heats and the heats of solution of the solids which were used in solution in the previous investigations, and also a speculation regarding a possible distribution of the degrees of freedom among their atoms.

2. Method of Determining the Specific Heats.-The calorimeter used in the determination of the specific heats was the form of Pfaundler's calorimeter already described. A liquid, either aniline or kerosene, was chosen as standard, which, according to the tests made with it, did not dissolve the solids. Appropriate amounts of this standard liquid were introduced into the calorimeter cups, such that when the solid was also introduced into the cup containing the smaller amount of liquid, the heat capacity, and therefore the rise of temperature, was about the same in both cups. Ordinarily 30 grams of the solid were used and the desired adjustment could be obtained without further trial by assuming 0.30 as the specific heat of the solid. The solids were introduced in the form of fine powder. Their specific gravities where such that when the liquid was stirred they were carried about with it, and easily and quickly took its temperature. The process of determining the relative heat capacities was carried out as has already been described, and from the results thus obtained the specific heats of the solids were calculated. For some reason which I have not been able to discover, but suspect to be the adhesion of a sheet of liquid to the walls of the cups, the rise and fall of temperature during the preliminary and final readings were not so regular as in the previous experiments with aqueous solutions, and the true initial and final temperatures had to be estimated. The uncertainty thus occasioned rendered the successive

determinations less accordant than those made with aqueous solutions, and the final results may be in error by two or three per cent. Errors may also have arisen if any of the solid was dissolved by the liquid used. These errors, if such there were, would generally have made the result obtained too large. As I carefully examined each substance about which there was any doubt by watching small crystals of it placed in the liquid and left standing for some days, I feel quite confident that no appreciable solution took place. This conclusion is confirmed by the fact that the temperature of the liquid containing the solid showed no evidence of any absorption of heat.

3. The Standard Liquids. - The results obtained depend upon the values taken for the specific heat of the standard liquid. When this was aniline, the specific heat was taken to be 0.5155. This is the value given by Griffiths<sup>1</sup> for 20°. The specific heat of the kerosene was obtained by comparison with nitrobenzol, the specific heat of which at 20°, from data given by Regnault, <sup>2</sup> is 0.336. The specific heat for kerosene thus obtained is 0.4573, between 14° and 25°. As a percentage error in the specific heat of the standard liquid introduces the same percentage error in the final result, and as these assumed specific heats are not likely in error by as much as one per cent., they may be taken as correct. As a test of the correctness of the value obtained for kerosene and of the general validity of the method, I determined the specific heat of water by using 11.33 grams of it, introduced into the cup containing 578.13 grams of kerosene, and comparing the heat capacity of the mixture with that of 600 grams of kerosene in the other cup. The specific heats obtained from two observations were 1.023 and 0.976, the mean being 0.9995. The deviations of these results from the mean show what I consider to be the probable range of error in the determinations made by this method.

4. Results. — In the following table are collected the results of the measurements. Column I. contains the molecular weights of the substances; Column II., their specific heats; Column III., their

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the solvent used was water. When two numbers are given the upper one was obtained with water, the lower one with alcohol, as the solvent. The temperature range was from  $14^{\circ}$  to  $26^{\circ}$ . The substances marked A were determined in aniline, those marked K, in kerosene. I have added some results obtained by other observers,

whose names are given below.

Substance.	1.	11.	111.	IV.
Cane Sugar.	342	0.301	103 <sup>1</sup>	152.8
Hydrous milk sugar, A.	360	0.298	107	147
Anhydrous milk sugar, A.	342	0.288	99	147
Maltose, A.	360	0.322	116	142.7
Dextrose, A.	180	0.313	56.3	78. <b>8</b>
Levulose, K.	,180	0.276	49.7	89.6
Mannite, A.	182	0.315	57.3	108
Dulcite, K.	182	0.283	51.5	97.5
Resorcin, K.	110	0.266	29.2	63.4
				56.8
Hydroquinone, K.	110	0.258	28.3	63.4
				56.8
Pyrocatechin, K.	110	0.313	34.4	75.5
-				56.8
Urea, K.	60	0.321	19.2	21
				28
Glycerine, liquid.	92	0.576	53²	54
Phenol, liquid.	94	0.561	52.7 <sup>3</sup>	71.5
-				51.4

I was not able to make successful observations either with acetamide or with phenol.

5. Discussion of the Results.—It appears from the results here presented that the molecular heats of isomers are not always the same. In the case of resorcin and hydroquinone, they probably are the same, the difference being not greater than might be accounted for by experimental error, and the exact equality of the molecular heats of these substances in solution, both in water and in alcohol, rendering a similar equality for the solids not improbable. The other pairs of isomers all show marked differences. considerably increased when it goes into solution. Urea is the only solid which exhibits an exception to this rule. The molecular heat for solid urea is possibly too low. It may not change at all, and at any rate it changes but little, when urea is dissolved in water. It is, however, increased by solution in alcohol. Liquid glycerine retains the same molecular heat when dissolved in water. Liquid phenol dissolves in alcohol without change; its molecular heat is increased by solution in water.

6. Possible Hypotheses Regarding Specific Heats of Solutions. — In one of my earlier papers on this subject I have given reasons for believing that the dissociated ions of an electrolyte, dissolved in water, are joined with groups of water molecules, whose specific heat is diminished by the combination. The calculation of the heat capacity of an aqueous solution of an electrolyte, on this hypothesis, leads to a term in the formula which represents the molecular heat of the undissociated portion of the electrolyte. This is, in most cases tested, greater than the molecular heat of the solid solute-In a few cases the two are equal. This change in molecular heat may be due to combination with a group of water molecules, whose specific heat is increased by the combination ; and a similar combination, leading to a similar change in the molecular heats, may occur in the case of non-electrolytes.

It is, however, also possible that the process of solution, in the case of non-electrolytes, involves a loosening of the bonds which confine the atoms in the molecule, so that the increase in the molecular heat is due to an increase in the degrees of freedom of the atoms. In what follows I shall adopt this hypothesis provisionally, and endeavor to construct with it a consistent scheme showing a possible distribution of degrees of freedom among the atoms of the various substances as solids and in solution.

7. Staigmüller's Formula. — A formula has been proposed by Staigmüller,<sup>1</sup> from which it is possible, on plausible suppositions as

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But if we consider Staigmüller's formula as established by its applicability to gases, we may use it to calculate the degrees of freedom of these molecules, and then see if they can be made to fall into any consistent scheme.

Staigmüller's formula represents the molecular heat at constant volume as the product of a constant,  $\lambda = 0.98835$ , and  $\vartheta$ , a quantity which he calls the "Wärmedimension," whose magnitude depends on the number of degrees of freedom possessed by the molecule. The "Wärmedimension"  $\vartheta$  is defined by the formula  $\vartheta = a + 2i$ , where *a* represents the number of variable coördinates, at the most six in number, which determine the position of the molecule, and *i* represents the number of those coördinates, determining the position of the atoms in the molecule, which are variable and which determine, therefore, the number of degrees of freedom possessed by the molecule because of the peculiarities of its atomic structure.

By means of this formula I have calculated the values of i for the different substances from their observed molecular heats, and have then assigned such degrees of freedom to the atoms in their molecules as will reproduce these values. The interest in the results lies in the general simplicity of the schemes adopted, and in the analogies which appear between isomers and between compounds of similar character. In view of the complexity of these molecules, it seems to me that any kinetic explanation of their molecular heats can only be got by some such method.

8. Degrees of Freedom of Solids. — In the following table are given the schemes adopted for the solid molecules. Column I. contains their chemical formulas; Column III., the values of i calculated from Staigmüller's formula; Column II., the values of i obtained by assigning to each of the atoms whose symbol stands at the top of the lettered columns the number placed under it. The molecular heats of the isomers differ by 6. I have, therefore, supposed that one of the differences between isomers consists in this, that the molecule of the one is rigidly bound in the crystal while that of the other is free. The values of i in the case of the substances marked with a star (\*) are obtained by setting a of the formula equal to zero.

Except in the cases of the liquid glycerine and liquid phenol

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Substance.	I.	C.	н.	о.	N.	п.	111.
Dextrose,	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	1	1	1		24	25.5
Levulose.*	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	1	1	1		24	25
Mannite.	C <sub>6</sub> H <sub>14</sub> O <sub>6</sub>	1	1	1		26	26
Dulcite.*	C <sub>6</sub> H <sub>14</sub> O <sub>6</sub>	1	1	1		26	26
Resorcin.*	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	1	1	1		14	14.
Hydroquinone.*	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	1	1	1		14	14
Pyrocatechin.	C <sub>H</sub> O	1	1	1		14	14.
Urea.	CON,H.	1	1	1	1	8	7
Glycerine, liquid.	C <sub>3</sub> H <sub>8</sub> O <sub>3</sub>	1	2	2		25	24
Phenol, liquid.	C H O	1	3	1		25	24

the supposition that the atoms have each one degree of freedom reproduces the numbers obtained from Staigmüller's formula very exactly.

9. The Sugars. — The sugars have been omitted from the above list. Their degrees of freedom cannot be reproduced on quite so simple a scheme. Some, but not all, of the atoms of one sort must have more than one degree of freedom. An examination of the structural formulas for the sugars shows that the carbon atoms appear in them in two groups, one of eight atoms and the other of four, differently connected with the other constituents of the molecule. We may assume that the atoms thus differently connected have different degrees of freedom. If this is done the schemes for the sugars are as follows :

Substance.	I.	C4.	C8.	н.	о.	п.	III.
Cane Sugar.*	C <sub>13</sub> H <sub>23</sub> O <sub>11</sub>	1	2	1	1	53	52
Anhydrous Milk Sugar.*	C <sub>11</sub> H <sub>21</sub> O <sub>11</sub>	2	1	1	1	49	50

The effect of the water of crystallization in ordinary milk sugar and in maltose cannot be represented without further hypotheses.

10. Dextrose and Levulose. — If we examine the structural formulas for dextrose and levulose, we find that one carbon atom in each is distinguished from the other five by being differently connected with the other constituents of the molecule. If we apply the same hypothesis as that just made for the sugars, by giving to this atom the degree of freedom 2, we find that i for dextrose and levulose becomes 25, and the most serious discrepancy of the table is removed.

#### No. 2.]

11. Degrees of Freedom in Solution. — Turning now to the case of the same substances in solution, we may find i by the same formula. In this case a is always to be set equal to 6, as the molecules in solution must be considered free. The larger values of the molecular heats obtained in solution make it necessary to assign to some of the atoms a larger number of degrees of freedom than 1. The following table, with the same conventions as in §8, contains the schemes adopted.

Substance.	I.	C.	н.	о.	N.	п.	<b>III.</b>
Dextrose.	C.H.O.	1	2	1		36	37
Levulose.	C <sub>6</sub> H <sub>11</sub> O <sub>6</sub>	1	2	2	1	42	42
Mannite.	C <sub>6</sub> H <sub>14</sub> O <sub>6</sub>	1	2	3		52	51.5
Dulcite.	C <sub>1</sub> H <sub>1</sub> O	1	2	2		46	46
Resorcin, water.	C.H.O.	1	3	2		28	29
Hydroquinone, water.	C.H.O.	1	3	2		28	29
Pyrocatechin, water.	C,HO,	2	3	2	1	34	35
" alcohol.	C.H.O.	1	3	1		26	26
Phenol, water.	СНО	2	3	2		32	33
" alcohol.	C, H,O	1	3	1		25	23
Urea, water.	CON.H.	1	1	1	1	8	8
" alcohol.	CONH	1	2	1	1	12	11
Acetamide.	C,H,NO	1	2	2	1	15	15
Glycerine.	C,HO,	1	2	2		25	24

For the sugars we make the same supposition as before and obtain the following schemes.

Substance.	I.	C4.	C8.	н.	о.	п.	ш.
Cane Sugar.	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	1	2	2	1	75	74
Milk Sugar.	C.1H22O11	2	1	2	1	71	71
Maltose.	H11022C11	2	1	2	1	71	69

12. Comments. — I may direct attention to the following points which will be observed on an examination of the foregoing tables :

(a) The number of degrees of freedom which are assigned to the atoms never exceeds three, that is, the atoms of these sorts and in these relations can be conceived of as material points.

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in water and in alcohol may be ascribed to differences in the degrees of freedom introduced by solution.

(d) The act of solution may be considered as involving a loosening of the bonds confining the atoms in the molecule, whereby the number of its degrees of freedom is increased.

The particular choice made, in the schemes here presented, of the numbers to be assigned to the several atoms, is not always the only one that may be made. It commends itself to me, however, because of the probability that the carbon atoms, around which the others are clustered, would be most restricted in their freedom, and so should have assigned to them, when possible, the lowest number.

13. Degrees of Freedom of Liquids. — A similar set of coincidences is exhibited by the molecular heats of organic liquids. A number of these are given in the following table, for which the data were taken from Landolt and Börnstein's tables. The molecular heats employed in the calculation of i by Staigmüller's formula are those given for the temperature nearest  $0^\circ$ , except when otherwise noted.

Substance.	I.	с.	н.	о.	п.	ш.
Formic acid.	CH <sub>2</sub> O <sub>2</sub>	1	2	2	9	9
Acetic acid.	C,H,O,	1	2	1	12	12
Methyl alcohol.	CH <sub>4</sub> O	1	1	1	6	6.5
Ethyl alcohol.	C,H,O	1	1	1	9	9.5
" 160°		1	3	2	22	22.5
Propyl alcohol.	C <sub>2</sub> H <sub>8</sub> O	1	1	1	12	12.5
Isobutyl alcohol.	C <sub>4</sub> H <sub>10</sub> O	1	1	1	15	15
Isoamyl alcohol.	C <sub>5</sub> H <sub>12</sub> O	1	1	1	18	19
Ethyl ether.	C4H10O	1	1	1	15	15.5
" 120°		1	2	2	26	26.5
" 180°		1	3	2	36	35.5
Oil of Turpentine.	C10H18	1	1	1	26	25
Hexan.	C <sub>6</sub> H <sub>16</sub>	1	1		20	18.5
Heptan.	C7H16	1	1		23	21.5
Octan.	C <sub>8</sub> H <sub>18</sub>	1	1		26	26
Hexadecan.	C <sub>16</sub> H <sub>34</sub>	1	1		50	53

14. Degrees of Freedom of Liquids.—In the following table are given similar schemes for the degrees of freedom obtained from Schlamp's observations <sup>1</sup> on liquids at 100°. Some other values are <sup>1</sup> Schlamp, Beiblätter, XX., 1896, p. 857.

Substance.	I.	C.	н.	ο.	N.	п.	: 111.
Nitrobenzol, 8°	C <sub>6</sub> H <sub>5</sub> O <sub>2</sub> N	1	2	1	1	19	18.5
" 100°		1	2	2	2	22	22
Aniline, 25°	C <sub>a</sub> H <sub>7</sub> N	1	2		1	21	21
" 100°		1	2	1	2	22	22.5
Benzol, 6°	C <sub>6</sub> H <sub>6</sub>	1	1			12	10
" 100°		1	2			18	16
Naphthaline.	C <sub>10</sub> H <sub>8</sub>	1	2			26	24.5
a-Naphthylamide.	C <sub>10</sub> H <sub>9</sub> N	1	2		3	31	31
Nitronaphthaline.	C <sub>10</sub> H <sub>7</sub> NO <sub>2</sub>	1	2	2	3	31	31
p-Toluidine.	C, H, N	1	2		1	26	26
o-Toluidine.	C, H, N	1	2	1	1	26	26

inserted for other temperatures, taken from Landolt and Bornstein's tables.

15. Comments.—It appears on an examination of these tables for liquids that their degrees of freedom can be represented by schemes similar to those used before. In particular:

(a) The molecular heats of these liquids at low temperatures may be described in most cases by assigning one degree of freedom to each atom of the molecule.

(b) The change in the molecular heats as the temperature rises may be ascribed to an increase in the degrees of freedom of their atoms.

16. Restatement of Hypothesis.— The relations exhibited in all these tables may be otherwise expressed by saying that the molecular heat of an organic substance is the sum of the heat taken up by the molecule as a whole and of the atomic heats of the atoms, these atomic heats, which are different in different circumstances and in different combinations, being equal to  $2\lambda$  multiplied by I, 2, or 3, or within one per cent. to 2, 4, or 6. The heat taken up by the molecule as a whole is in most cases equal to  $6\lambda$ , or within one per cent. to 6. The slight discrepancies which appear when this scheme is worked out may be explained by the distinction introduced by Jeans<sup>1</sup> between principal and subordinate degrees of freedom.

17. Degrees of Freedom of Vapors. — It is apparently a general rule that the molecular heats of vapors are less than those of the liquids from which they are formed. In terms of our present hy-<sup>1</sup> Phil. Trans., Vol. 196, A, p. 397.

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pothesis, the degrees of freedom of a molecule are more numerous in the liquid than in the vapor. This may be rendered possible by the comparative balancing of the forces acting on an atom in a liquid due to the presence of neighboring molecules. When the molecule escapes from the liquid on evaporation this action no longer takes place and the atoms fall back into more restricted relations. Calculations from such scanty data as I have at hand show that similar schemes to those already presented may be constructed for the vapors. The number of degrees of freedom, calculated from Staigmüller's formula, comes out so low in each case, that it is necessary to suppose that the carbon atoms in the molecules of these vapors lose their freedom entirely.

18. Heats of Solution. Method. - I have determined the heats of solution in water of the organic solids previously studied, to see if any relation could be shown to exist between them and the estimated change in their degrees of freedom brought about by solu-The determination was made with the silver cups of my tion. calorimeter, fitted with covers for holding the thermometers and the silver paddles. A portion of the cover was hinged and could be raised to introduce the solid. Each cup was filled with 750 grams of distilled water at about the room temperature. The substance to be examined was finely powdered, except in a few cases of very soluble substances, 20 grams of it were weighed out, and a thermometer bulb covered with it, The cups were then placed in position and the temperatures of the water in both observed, until the change from minute to minute seemed uniform and the same in both. The temperature of the powder was then read, and the powder poured into one of the cups. The temperatures were then read at frequent intervals until by the uniform and equal rise of temperature in both cups it was evident that solution was complete. By the help of the control cup, in which the pure water changed its temperature steadily by reason of radiation and the agitation by the paddles, the change of temperature due to the same causes in the other cup could be determined, and a simple

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the substance, both as solid and in solution, from my previous measurements, and knowing the heat capacity of the cup, it is easy to calculate the heat developed by the act of solution. In every case but that of glycerine heat was absorbed, or the heat of solution is negative.

19. Heats of Solution. Results. — The results of the experiments are given in the following table. Because of the small amount of material on hand, most of the substances were tested only once. From the results obtained when the experiments were repeated, it apppears that the results in general are not in error by more than one or two per cent.

Substance. I. 11. III. 19.7 Cane Sugar. - 3.6 -1231Hydrous milk sugar. - 11.5 - 4140 21.6 Anhydrous milk sugar. - 7.4 - 2530 19.2 Erdmann's milk sugar. - 1231 - 3.6 19.3 Maltose. - 9.75 - 3510 19.8 Dextrose. - 13.02 - 2344 18.7 " - 13.09 - 2356 18.9 Levulose. - 10.6 - 1908 18.7 Mannite. - 28.2 - 5132 18.7 Dulcite. - 36.7 - 6679 18.9 - 34.1 - 3751 Resorcin. 18.2 \*\* - 35.3 - 3883 20.0 - 41.2 - 4532 Hydroquinone. 18.5 " - 41.8 - 4598 20.0 Pyrocatechin. - 31.3 - 3443 19.5 - 31.0 - 3410 19.0 Phenol. - 30.6 - 2876 19.9 Urea. - 60.4 - 3624 18.6 + 1290Glycerine. + 14.0 20.0

In the table, Column I. contains the heat developed by I gram of

the substance dissolved in 37.5 grams of water; Column II., the product of this quantity of heat and the molecular weight of the substance, or the heat developed by a gram molecule of the sub-stance dissolved in 37.5 times its weight of water; Column III., the

heat developed by solution, just as they do with respect to their molecular heat. Even the isomers resorcin and hydroquinone, which in their specific heat relations are so similar, have different heats of solution. Except in the case of the isomers dextrose and levulose, the one of a set of isomers which dissolves with most difficulty has the largest negative heat of solution.

No general relation between the heats of solution and the estimated change in the number of degrees of freedom has been detected. The heats of solution, depending as they do on the work done in separating the molecules of the solid, and perhaps on the negative work done by combination of these molecules with those of the solvent, as well as on the change in the degrees of freedom within the molecule, should not of necessity exhibit any such relation.

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# ON A MECHANICAL METHOD FOR TRACING THE CURVES $x^{k}y = \text{CONSTANT}$ .

BY EDGAR BUCKINGHAM.

I. For students who are studying the properties of gases — particularly in connection with steam, gas, and air engines — it would be of advantage to have some means, less laborious than computation and plotting, for constructing the curves  $x^{k}y = C$ , which have, approximately, the shapes of the adiabatic lines in the (p, v) plane. Since I do not remember seeing any mention of an instrument for this purpose, I have devised one; and though I have not had facilities for constructing a working model, I think that the scheme may interest some readers of the PHYSICAL REVIEW.

The first object in such a design is simplicity of construction. It is therefore obvious that the relative motions of the various parts of the instrument should, so far as possible, be motions of rotation, and that the number of sliding motions should be reduced to a minimum. For it is easier to do good work quickly on the turning lathe than on the planing, shaping, or milling machine. There must, furthermore, be the possibility of taking up, by springs, all lost motion or back-lash, at the various contacts.

2. By differentiating the equation  $x^k y = C$ , we get

$$kx^{k-1}ydx + x^{k}dy = 0,$$

$$\frac{dy}{dx} = -k\frac{y}{x}.$$
(1)

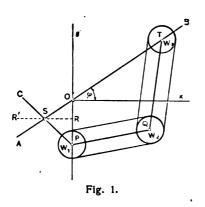
whence

The curve must therefore be drawn in such a way that its slope is equal to -k(y/x).

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axis through the tracing point and perpendicular to the plane oxy, that the motion of advance of the tracing point is the proper one, satisfying equation (I). The problem is, then, to move some bar about a fixed axis so that it shall have the direction required for the tangent to the curve at the point occupied by the tracer; and then, to find a means of transmitting this *direction* to the tracing carriage, so that the planes of rotation of the guide-wheels shall be always parallel to this bar. The problem may be solved in the following manner:

A straight bar AB is pivoted at the origin of coordinates o. A rail RR', perpendicular to the axis of y and below the origin, acts



as guide to a carriage S, which carries a double pivot with its axis perpendicular to the plane *oxy* and passing through the line RR'. The lower part of this double pivot turns directly in a bearing in the carriage, and has, perpendicular to its axis, a hole through which the bar AB can slide freely but without shaking. The upper part of the pivot turns in a bearing in the lower part and has, per-

pendicular to the common axis of both parts of the pivot, a hole through which the straight bar PC slides while rotating about the pivot P. The pivot P is fixed for any given value of the constant k, but can be set, by motion along the negative axis of y, so as to give the distance  $\overline{RP}$  any value between  $\overline{RO}$  and 1.67  $\overline{RO}$ .

Upon the bar AB is a slide carrying on the side nearest the tracing surface, a pivot T. The tracing point, supported and guided in its motion by two coaxial guide-wheels, touches the tracing surface in the intersection with that surface, of the axis of the pivot T. The frame which contains the bearings of the guide-wheels turns upon the pivot T, concentrically with the tracing point.

An arm PQ, pivoted at P, is jointed at Q to the arm QT which turns about T; thus the pivot T does a double duty but has not the complications of that at S. Concentric with P is a grooved pulley  $W_1$ , rigidly connected with the arm *PC* and sharing its rotations. Concentric with *Q* is a doubly grooved pulley  $W_2$ , rotating freely on a prolongation of the pivot *Q*. Concentric with *T*, and rigidly connected with the carriage which holds the tracing point and guide-wheels, is a third grooved pulley  $W_3$ . These three pulleys are of equal diameter. An inextensible band passes, with friction, around  $W_1$  and  $W_2$ , and another similar band around  $W_3$  and  $W_3$ .

3. Suppose P to have been so fixed on -oy, that RP/RO = k. If the bar AB rotates about O, the carriage S slides along the rail RR', while AB itself slides through S, as does PC. In this way, the intersection of the projections of PC and AB on the plane oxy lies constantly on the fixed projection of the line RR'. For the sake of brevity, we will now regard the figure as a purely geometrical one drawn in the plane oxy.

Since AB passes through the tracing point T, we have

tan angle 
$$\overline{RSO} = \frac{RO}{SR} = \frac{y}{x}$$
.

But

tan angle 
$$\overline{RSP} = \frac{RP}{SR} = -k \frac{RO}{SR} = -k \frac{y}{x}$$

Therefore by equation (1) we have

tan angle 
$$RSP = \frac{dy}{dx}$$
;

or, in other words, CSP has the direction of the tangent drawn to the required curve at the point occupied by the tracer T.

If the frame which holds the guide-wheels and tracing point be so rotated about the pivot T, that the axis of the guide-wheel is at every instant perpendicular to PC, the tracing point will be so directed over the surface, that as the bar AB rotates about O, the required curve is described. This, as is easily seen, is accomplished by the bands about  $W_1$ ,  $W_2$ ,  $W_3$ , if there is no slip and if the planes of rotation of the guide-wheels have once been set parallel to PC. The whole object of the arms PQ and QT is to provide an extensible band-connection between P and T. If AB be now rotated about O, the tracing point, while sliding with its pivot along AB, will trace the curve  $x^{k}y = C$ ; and the value of C may be varied by lifting T from the tracing surface, sliding it along the radial arm AB, and finally readjusting the axis of the guide-wheels so that it shall again be perpendicular to PC.

4. Though this instrument is simple compared with several other preliminary schemes which occurred to me, it has several places where possible lost motion must be taken up. The arms PQ and QT may be made telescopic and extended by compressed spiral springs so as to keep the bands (fine brass wire) always in a state of tension; or, if the pulleys are small in diameter, the bands may be made elastic by the insertion of spiral springs. A spiral spring acting toward the right on the carriage S will take up the lost motion of AB and PC at S. A coiled spring about the pivot T, between the slide and the rotating tracing carriage, will take up lost motion of rotation. The looseness of S on RR', and of T on ABmay be taken up in various ways too obvious to need mention.

The mechanical construction may be simplified by making the main radial arm AB, and the secondary or tangent arm PC, double, each consisting of a pair of parallel bars (brass tubes). In this case, only a single pivot is needed at S and it may be fixed rigidly upon the carriage which slides along RR'. Two slides, one on AB and the other on PC, each bored to fit over the pivot S will then accomplish the desired result.

It is obvious that whatever be the available lengths of the rail RR' and of the arms OA and PC, the action of the mechanism will become stiff and inaccurate when RS is large. Hence, supposing RR, OA and PC to be indefinitely long, the minimum value of  $\varphi$  to be attained in practice, will decrease as the accuracy of construction increases and as the friction — especially the sliding friction at S and T— diminishes.

A similar limit is set to the maximum practicable value of  $\varphi$  by the sliding friction at T; but, on the whole, the instrument as here planned will be more effective for large than for small values of  $\varphi$ . If the parts of the curve nearer the axis is of x, that is, those for which  $\varphi$  is small, are of the greater importance, the scheme may easily be so altered as to interchange the limitations to which  $\varphi$  is subject in the vicinity of O and  $\pi/2$ .

#### No. 2.] METHOD FOR TRACING CURVES.

It may be noticed, in conclusion, that since the pivot P may be so placed as to make RP equal to (or even less than) RO, the instrument may be adjusted for drawing the equilateral hyperbolas xy = C, which give an approximate representation of the isothermal lines of the gases in the pv plane, for values of the temperature which are above and not too near the critical temperature.



#### PROCEEDINGS

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# $C_{p}$ in Liquids and the $\alpha$ of van der Waals in the Case of Water.

#### BY EDWIN H. HALL.

THE specific heat,  $C_{v}$ , of liquids at constant volume is a subject which deserves more attention than it generally receives. For example, Nernst on p. 234 of his *Theoretische Chemie*, 2d edition, says: "If a fluid were kept at constant volume during heating, then (provided the theory of van der Waals is strictly applicable to it) its specific heat would have to be just as great as that of its vapor, the latter also, of course, being taken at constant volume," and he appears to argue in favor of the general truth of this relation, without, however, giving any specific instance of  $C_{v}$ , except in the case of water at 4° C., where, obviously,  $C_{v} = C_{v}$ .

It is easy to get a convenient formula for  $C_{v}$  in terms of  $C_{p}$ , e, the coefficient of expansion at constant pressure, k, the coefficient of compressibility at constant temperature, v, the specific volume, and T, the absolute temperature. This formula<sup>1</sup> is,

(1) 
$$C_v = C_p - \frac{e^2 v T}{k}$$
, or  $C_v = C_p + \frac{\left(\frac{dv}{dT}\right)_p^2}{\left(\frac{dv}{dp}\right)_T}T$ .

If we apply this formula to the case of water at temperatures above  $4^{\circ}C_{\cdot}$ , we find that  $C_{\bullet} < C_{p}$ . At  $50^{\circ}$  C., for example,  $C_{p} \div C_{\bullet} = 1.03 + ;$  but at this temperature, and probably at much higher temperatures,  $C_{\bullet}$  for liquid water is still much greater than  $C_{\bullet}$  for water vapor.

<sup>1</sup> Mr. L. D. Hill, of Cambridge, finds that Combes (Theorie de La Chaleur, 1863)

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By imagining unit mass of a liquid put through a very small cycle consisting of an isothermal, an isopiestic, and an isometric, it is easy, with the use of equation (1), to derive the following expression for  $\Delta E$ , the internal latent heat of expansion at constant temperature through a small increase of volume  $\Delta v$ :

(2) 
$$\Delta E = \left(\frac{e}{k}T - p\right)\Delta v.$$

The argument thus far has been thermodynamic and rigid. It has now brought us to a place of uncertainty and of interesting speculation. If we assume that  $\Delta E$  is merely the work of overcoming molecular attraction and that, as in the theory of van der Waals, this attraction is expressed by  $a/v^2$ , where a is a constant, we can find a value of a in the case of an expanding liquid by means of the equation,

Applied to water at  $15^{\circ}$  C. this equation gives approximately  $a = 933 \times 10^{\circ}$ . If now, using this value of *a*, we calculate the amount of energy required to overcome the molecular attraction in the evaporation of water at  $15^{\circ}$  C., we find that only about one twenty-fifth part of  $\lambda$ , the internal latent heat of evaporation is thus accounted for. If we make a similar calculation at  $50^{\circ}$  C., we find, from the expansion of the liquid,  $a = 3,720 \times 10^{\circ}$ , large enough to account for nearly one sixth part of  $\lambda$  at this temperature. At  $100^{\circ}$  we get in the same way a = perhaps  $6,400 \times 10^{\circ}$ , accounting for nearly one third of  $\lambda$ . At the critical temperature the discrepancy should, apparently, entirely disappear.

The theory of van der Waals requires that, for any given temperature, a and the mean energy of *translatory* molecular motion shall be constants. It apparently does not require that the *whole* energy of molecular motion shall be a function of temperature only. Apparently we could account for the thermodynamic relations of water and water vapor by means of the following assumptions:

1. That, at temperatures below the critical, a is independent of volume but increases with temperature.

2. That, at temperatures below the critical, the total energy of molecular motion increases during evaporation, though the energy of translatory

#### THE HEAT OF VAPORIZATION OF NITROGEN.

#### By J. S. SHEARER.

IN connection with the determination of the heat of vaporization of air it was found desirable to find this constant for each constituent. The result for oxygen has been reported at a previous meeting. For atmospheric nitrogen it was found that 49.8 calories per gram are absorbed in vaporization. As the result for oxygen was 60.9 it follows that the heat of vaporization of air should increase as it becomes richer in oxygen.

# The Heat of Vaporization of Air as Related to Its Composition.

#### BY J. S. SHEARER AND F. R. STRAYER.

SINCE there is a considerable difference in the heats of vaporization of oxygen and nitrogen the writers sought to determine whether or not the energy used is the same as would be required to vaporize the same amount of the unmixed liquids. The composition of the vapor phase was found by pyrogallol absorption, and percentages of oxygen and total vapor produced were plotted as coördinates. The area of this curve gives the total oxygen in the original liquid air, and the composition of the liquid phase at any point is readily found. The results would indicate that the heat required is probably the same as would be required to vaporize the constituents separately.



#### NOTE.

Carl Anton Bjerknes. - Carl Anton Bjerknes was born in Christiania on the 24th of October, 1825. He interested himself at an early day both in mathematics and physics, but at the University of Christiania, where he studied in 1844, there was no advanced instruction in these subjects. He was therefore compelled to devote himself to mineralogy instead and in 1849 he was appointed to a position in the Silver Mining Works at Kongsberg. During this period he continued his mathematical studies as best he could and during 1855 and 1857 he received a public stipend with which to study in Paris and Goettingen. Upon his return he became a docent in mathematics at the University of Christiania. In 1863 he was appointed reader and in 1866 professor of applied mathe-In 1869 he was transferred to the chair of pure mathematics matics. which he occupied up to the time of his death.

Bjerknes's older published work was in the realm of pure mathematics, but he is best known for his investigations in hydrodynamics. A study of the works of Euler had early led him into the ranks of the opposition to the law of action at a distance, which in his younger days was almost universally accepted. While a student at Goettingen he attended the lectures of Lejeune-Dirichlet, in the course of which the solution of the hydrodynamic problem of the movement of a sphere in a fluid was pre-This solution led to the conclusion, very surprising at first sight, sented. that the sphere would move through the fluid with constant velocity and without meeting with resistance; a result which brought Bjerknes to the conception that the principle of inertia would hold with the same exactitude in a space filled with fluid as in vacuo. He was thus led to attack the problem of the simultaneous movement of several spheres in a fluid and to the question whether their movements would not mutually influence each other. Such an influence would obviously present the appearance of action at a distance between sphere and sphere and it was his purpose to determine whether these apparent actions at a distance were not analogous to those observed in nature. Greatly hindered by illness and other circumstances he was able to attain to the solution of this problem for the first time in 1868 when he found that such apparent actions at a distance really took place between the spheres and that with the single striking exception that the law of equality of action and reaction did not hold, they possessed all the fundamental properties which 126

we are accustomed to assume in the ordinary mechanics of action at a distance in nature. Further penetration into the nature of the forces which Bjerknes had discovered was first attained in 1875, at which time he found that these forces could be divided into two parts, one of which produced an invisible, the other visible motions. For the latter the principle of equal action and reaction held true so that this force possessed all the fundamental properties ascribed to the forces of nature in mechanics. This force which produced visible motions showed moreover the most extraordinary similarity to those producing action at a distance in electrostatics and magnetism ; but always with opposite sign.

With the applications of this remarkable hydrodynamic analogy to electrical and magnetic phenomena Bjerknes subsequently occupied himself up to the time of his death; extending the comparison further and further and verifying all the principal results by experiment. The experimental work confirmed in the most striking manner the results of his computations and showed that these hydrodynamic actions at a distance have in every respect the appearance of interaction between electrified or magnetized bodies but always with the direction of the force reversed. Bjerknes was not, unfortunately, to have the satisfaction of laying his results before the scientific world except through the chance exhibition of some of his experiments or by means of preliminary communications concerning the same. The latest mathematical discussion which he published on this subject was printed in 1876. His extraordinary conscientiousness and excessive criticism of his own labors, taken in connection with the extraordinary difficulty of the subject, prevented him from working out in complete form the great treatise on his discoveries which he had planned and the editing of this work was accordingly taken up by his son, Professor V. Bjerknes,<sup>1</sup> of Stockholm. The investigations have not nearly all of them as yet appeared in the published form, but a few months before his death, which occurred on the 20th of March, 1903, Bjerknes had the pleasure of seeing the first portions of the complete work in print.

#### V. BJERKNES.

<sup>1</sup>V. Bjerknes: Vorlesungen über bydrodynamische Fernkräfte nach C. A. Bjerknes' Theorie; Leipzig, 1900-02.

### NEW BOOKS.

Handbuch der Spectroscopie. Von H. KAYSER. Zweiter Band; pp. xi + 696. S. Hirzel, Leipzig, 1902.

The second volume of Professor Kayser's Manual fully meets the expectations aroused by the appearance of Volume I. We find the same breadth of treatment and the same extraordinary completeness in dealing with the extensive literature of this subject. No contribution of any importance seems to have escaped the notice of the author and what is more remarkable, when one considers the enormous number of papers which have appeared, each piece of work has been read and its value estimated with fairness and good judgment. The author gives his opinion with great frankness and freedom, but his criticisms are tempered throughout with fairness and his dictum concerning many difficult points which have been in the past or still are subjects of dispute will command respect, and in general, acquiescence on the part of those who read his admirable summaries. A good example of Professor Kayser's ability to deal with such matters may be seen in his discussion of the relative claims of Balfour Stewart and Kirchhoff in the establishment of the law of emission. Stewart's failure to produce a conclusive and completely generalized demonstration of what we know as Kirchhoff's law is clearly brought out but the value and the significance of his extended labors in this field are fully and appreciatively recognized. Another instance of the author's skill in the handling of a vexed question is found in the review of the literature dealing with the phenomena of the first appearance of visible radiation from a hot body (pages 41-48). Kayser points out quite rightly that the later observations of Weber, Stenger, Ebert, Emden, etc., do not lead to an abandonment of the earlier views but that they serve rather to establish certain physiological phenomena of vision unrecognized by Draper, Kirchhoff and their contemporaries. There can be little doubt, in view of the newer researches, of the correctness of Violle's contention that the reception of light, with gradual rise of intensities precedes the reception of color. Nor is it strange considering the enormously greater luminosity of the rays lying in the middle of the spectrum that these should first be capable of producing color sensation in snite of the greater energy of the longer many langths The perature does not increase uniformly as the wave-length decreases, in strict accordance with the views of Draper but that in certain regions intensity increases faster than in others so that the phenomenon is a more complicated one than was once imagined.

In his brief discussion of the phenomena generally classed under the head of fluorescence the author makes use of the very appropriate terminology invented by Wiedemann and describes these types of radiation under the title of *luminescence*. In the important chapters on the principle of Doppler and upon the Zeeman effect he has availed himself of the services of Dr. Konen and Professor Runge respectively; a choice which justifies itself in the admirable treatment given to these subjects.

One of the most important chapters in this volume is that which deals with the structure of line spectra, the grouping of lines, their occurrence in systems or series and the laws which appear to govern the arrangement of such lines. This is a domain in which we are likely to see important developments in the near future and the gathering together of the work already done is at this time peculiarly serviceable and useful.

All students in light and especially those who have occasion to work with the spectrum will look forward to the remaining volumes of Professor Kayser's hand-book with the greatest interest and confidence. No such comprehensive work has ever been attempted in this field of research. Its value to those who are striving to advance our knowledge of spectroscopy is beyond estimate. E. L. N.

*Electrical Problems.* By W. L. HOOPER and R. T. WELLS. Pp. i + 170. Boston, Ginn & Company, 1902.

This work comprises a particularly clear set of problems well suited to give concrete illustration to all the more important principles of electricity and magnetism. The problems are well arranged and selected so as to give to abstract relations a reality which can otherwise be attained only by a long experience with electrical apparatus and engineering calculations. No theory is given, but suggestions are made which for the most part are exceeding apt. Practice with the problems in this book should give the student not only facility and accuracy in making calculations, but a much clearer conception of the fundamental principles of electrical engineering.

F. BEDELL.



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## THE

# PHYSICAL REVIEW.

### DIFFUSION AND SUPERSATURATION IN GELATINE.

BY HARRY W. MORSE AND GEORGE W. PIERCE.

#### I. INTRODUCTION.

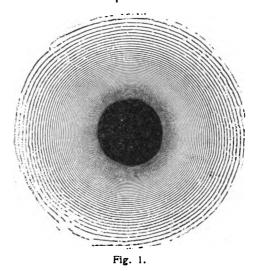
THE German photographer, R. Ed. Liesegang, in the course of a research on chemical reactions in gelatine<sup>1</sup> discovered a phenomenon which Ostwald cites as evidence that there exists a definite limit beyond which, at a given temperature and pressure, the supersaturation of a solution cannot be carried. We have undertaken an experimental study of this subject by a method based on Liesegang's discovery.

Liesegang's experiment was as follows : a glass plate was covered with gelatine impregnated with potassium chromate. The plate was laid horizontal, and upon it a drop of silver nitrate was placed. The silver nitrate diffused slowly out into the gelatine, reacted with the potassium chromate, and formed a precipitate of silver chromate. The silver chromate, instead of growing continuously in the gelatine, as diffusion of the reacting substances went on, formed in distinct rings about the drop, as shown in Fig. 1. The formation of the precipitate in distinct rings is clearly a phenomenon of supersaturation. We have undertaken certain measurements of these rings in the hope of being able to obtain from them some understanding of the conditions that exist in supersatuing substances, and to estimate the limit of supersaturation attained when the solid phase is not present—the so-called "Metastable Limit" of Ostwald.

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Before proceeding to the experiments we shall give certain definitions and explanatory paragraphs from Ostwald's Lehrbuch.<sup>1</sup>

"Between a solid substance and its supersaturated solution an equilibrium is formed, which depends on the nature of the substances, the temperature and the pressure. If we leave out of account the



influence of the pressure, for every temperature there is a definite equilibrium. This is evidenced by a definite concentration up to which the solid substance dissolves. \* \* \*

"When the solid phase is not present the concentration of the dissolved substance is arbitrary. The limit of concentration on one side is zero; on the other side the limit is a concentration difficult to determine, which, however, is greater than that of the equilibrium with the solid phase.

"Solutions whose concentrations exceed the concentration of saturation with a possible solid phase are called supersaturated with reference to this solid phase. \* \* \*

"The simplest way of abtaining a supersaturated solution is to

the solvent a solution that is more concentrated than a saturated solution at the temperature of the experiment. In most cases the temperature required to produce supersaturation is higher than the temperature of the experiment, but it can also be lower in cases where the solubility decreases with increase of temperature.

"A better way to obtain supersaturated solutions, since it is thereby easier to exclude germs of the solid phase, is to employ reactions that produce in the solvent concentrations of the substance in question in appropriate amount.

"Among supersaturated solutions there are some which under definite conditions can be kept indefinitely, if germs are excluded, without formation of the solid phase. Such solutions are called Metastable.

"On the other hand, there are some solutions in which, even when germs are excluded, the solid phase appears after a short time. Solutions of this type are called Labile.

"Metastable solutions always show smaller concentration than the labile solutions of the same substances. By increase of concentration, therefore, a metastable solution goes over into a labile condition. The concentration at which the transition occurs is called the metastable limit.

"The metastable limit is, in the first place, dependent on the nature of the substances, on the temperature, and on the pressure. In addition it is influenced by various other circumstances not yet explained. At the present time (1899) it is hardly possible to speak more definitely concerning the value of the metastable limit and the methods of determining it."

It is in connection with this discussion in the *Lehrbuch* that Ostwald cites the sharpness and regularity of Liesegang's rings as evidence that the metastable limit is something definite. But so far as we are aware, no attempt has hitherto been made to study Liesegang's rings quantitatively, and to obtain from them the actual numerical value of the metastable limit. In fact, so far as we are aware, there has not been published a determination of the metastable limit in any case. We quote further Ostwald's explanation<sup>1</sup> of the formation of Liesegang's ring-system:

<sup>1</sup> Lehrbuch, II., 2, 778.

"By the diffusion of the silver salt into gelatine containing chromate a solution is formed which is supersaturated with respect to silver chromate; precipitation does not take place until the metastable limit has been exceeded. This naturally happens simul-

> taneously in a circle concentric with the drop. Silver chromate, in relation to which the neighborhood of the ring is supersaturated, deposits on the precipitate already formed and strengthens it; this continues until the soluble chromate has been removed from the neighborhood and deposited on the precipitate. The silver salt, diffusing on farther, supersaturates a new circular region, and the process repeats itself. Since the silver nitrate becomes more dilute by diffusion, the critical concentration at which precipitation begins is reached later and later, and the rings form farther and farther apart."

> Liesegang has also shown that if the potassium chromate in gelatine is put into a capillary *tube* instead of being spread upon a plate, analogous phenomena occur when one end of the tube is dipped into a solution of silver nitrate. The precipitate in the tube is formed in layers, or discs, perpendicular to the axis of the tube (Fig. 2).

This phenomenon of the formation of a precipitate in rings on a plate or in discs in a tube is not confined to the case of a reaction between silver nitrate and potassium chromate. Liesegang found such a formation of a precipitate in the case of mercurous chromate, lead chromate and Prussian blue, in the familiar reactions which give these precipitates. We have found that with a proper choice of concentrations rings are also formed in the following cases :

ABLE	1.

Diffusing Subs.	Subs. in Gell.	Precip.	Nature of Rings.
Pb(NO <sub>3</sub> ) <sub>2</sub>	Na <sub>2</sub> SO <sub>4</sub>	PbSO4	Fine. White. Close together.
AgNO <sub>3</sub>	K <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	Ag <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	** ** ** **
"	Na <sub>2</sub> CO <sub>3</sub>	Ag <sub>2</sub> C() <sub>s</sub>	Thick. Far apart.
"	Na, HPO	Ag <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	Fine. White.
"	NH <sub>4</sub> CNS	AgCNS	
"	KBr	AgBr	
$Co(NO_3)$ ,	NaOH	Co(OH),	Gelatinous. Thick.
BaCl,	K <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	BaC,O,	Distinctly crystalline.
HgNO	KBr	HgBr	Fine. White
FeCl,	Na,CO,	cõ,	Gas bubbles.

Fig. 2.



It is our intention to give a more extended description of the various reactions in this table at some future time. At present, however, in order to discuss the quantitative aspect of the problem, we shall confine our attention to a single case — the formation of supersaturation rings of silver chromate.

The experiment was as follows: A capillary tube of diameter .5 to 1 mm. was filled with a 1/75 or a 1/150 normal solution of potassium chromate in gelatine. After the gelatine had set, a piece of the tube about 5 cm. long, obtained by breaking the tube under water so as to expose a fresh moist surface of the gelatine, was plunged vertically into a water solution of 2N, N or N/2 AgNO, contained in a flat-walled glass vessel. By means of a cathetometer carrying a microscope of low power we watched the formation of the precipitate. After a certain period of time, depending on the concentration of the solution, the precipitate near the advancing front of the diffusing substance began to appear in layers, or discs, widely separated in comparison with their thickness. These discs appeared suddenly as sharp thin films, so that the time of their appearance could be determined with accuracy. The *distance* of each disc from the bottom of the tube was read off on the cathetometer. Measurements so obtained are recorded in the appended Tables IV. to XXIV. The experiment was conducted in a constanttemperature room, which, except for the short time necessary for the taking of readings, was kept dark or dimly lighted to exclude the possible action of light in hardening the gelatine.

The reaction is in accordance with the formula :

$$2AgNO_3 + K_2CrO_4 \leq Ag_2CrO_4 + 2KNO_3$$

The advance of the reaction in the one sense or the other is conditioned upon the concentration of the active substances. For equilibrium the concentrations must satisfy the quantitative relation :

$$A_{g^{2}}^{+2} \times C\bar{r}\bar{O}_{4} = K \cdot Ag_{2}CrO_{4}, \qquad (a)$$

where  $A_g^+$  and  $CrO_4$  are the concentrations of the silver ion and the chromate ion respectively,  $Ag_2CrO_4$  the concentration of the undissociated silver chromate in solution, and K the equilibrium con-

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stant. When the solid phase is present the undissociated silver chromate in solution must be in equilibrium with the solid phase, and must, therefore, be present in constant amount. In saturated solution, therefore,

$$Ag^{+2} \times C\bar{r}\bar{O}_{4} = k, \qquad (1)$$

where k is the solubility product.

Now in supersaturated solution the mass law (Eq. a) is probably still true, and the question arises : Is there a relation similar to (1), with, however, a different constant product that defines the limit of supersaturation?

Is there a formula of the form

$$Ag^{+2} \times \bar{CrO}_{4} = H$$
 (2)

for the condition that the concentrations must satisfy when the precipitate just begins to form in the *absence* of the solid phase?

#### II. THEORETICAL CONSIDERATIONS.

We can calculate the value of H in equation (2) provided we can calculate the values of the concentrations of the two ions at the point and at the time at which a ring begins to appear. We propose to attempt to obtain the values of these concentrations by the mathematical theory of diffusion. To avoid possible confusion from the use of general terms we shall take the specific case in which silver chromate is the precipitated substance; the same analysis will, of course, apply to any other case.

Suppose a capillary tube (Fig. 3), containing, in gelatine, a dilute solution of potassium chromate, to be plunged at the time t = 0 into a vessel containing a strong solution of silver nitrate; let the distance x be measured from the end of the tube, with its positive direction along the axis of the tube; let u be the concentration of the  $A_g^+$  ion at the point x at the time t, v the corresponding value for the  $CrO_4$  ion. At the instant the tube is plunged in,

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As a first approximation we may assume that the dissociation of the  $K_2CrO_4$  is complete, since this substance is present in very dilute solution for values of x and t such as we shall need to consider; the concentration of the silver salt in the tube will also be small and we shall at present consider it to be completely dissociated. Later we can see how to correct the error introduced by

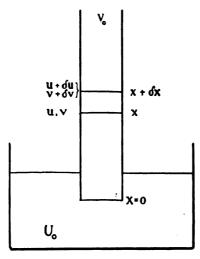


Fig. 3.

this assumption. Thus if we measure concentrations in grammolecules, the concentration of the  $A_g^+$  ion is the same as that of the AgNO<sub>3</sub>, and the concentration of the  $CrO_4$  ion is that of the K<sub>2</sub>CrO<sub>4</sub>. We are to calculate the two concentrations from the diffusion of AgNO<sub>3</sub> and K<sub>2</sub>CrO<sub>4</sub>.

The diffusion constant is defined as the number of units of mass that will go through a unit cross-section in a unit of time under head of unit gradient of concentration. Let  $a^2$  (essentially positive) be the diffusion constant of silver nitrate; then the quantity of silver nitrate that will cross a section S of the tube at a distance x from the origin in a time  $\partial t$  is the diffusion constant x gradient x time x area of cross-section. Therefore,

$$Q = -a^2 \frac{\partial u}{\partial x} \cdot \partial t \cdot S.$$
(3)

The quantity crossing a section at a distance  $x + \partial x$  is

$$Q + \frac{\partial Q}{\partial x} \cdot \delta x = -a^2 \frac{\partial u}{\partial x} \delta t \cdot S - a^2 \frac{\partial^2 u}{\partial x^2} \cdot \delta t \cdot \delta x \cdot S.$$
(4)

The accumulation of silver nitrate in the region between x and  $x + \partial x$  is the difference of these quantities,

$$a^2\frac{\partial^2 u}{\partial x^2}\delta t\cdot \delta x\cdot S.$$

This accumulation may also be expressed as change of concentration multiplied by the volume =  $\partial u \cdot \partial x \cdot S$ ;

$$\therefore \ a^2 \frac{\partial^2 u}{\partial x^2} \delta t \cdot \delta x \cdot S = \delta u \cdot \delta x \cdot S,$$

whence, dividing by  $\delta t \cdot \delta x \cdot S$ 

 $a^{2}\frac{\partial^{2}u}{\partial x^{2}} = \frac{\partial u}{\partial t}$ (5)

This is Fick's Law.<sup>1</sup>

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Analogous considerations give us an exactly similar equation for the concentration of the  $Cr\bar{O}_4$  ion at the point x and time t; namely,

$$b^2 \frac{\partial^2 v}{\partial x^2} = \frac{\partial v}{\partial t} \tag{6}$$

where  $b^2$  is the diffusion constant for potassium chromate.

In deriving these equations we have made the assumption that the formation of earlier precipitates does not materially affect the head under which the ions accumulate for the formation of new precipitates. If we make this assumption we can solve the problem completely.

Equations (5) and (6) are exactly alike, but their solutions will be different because they have to satisfy different initial conditions in the two cases. The lower end of the tube was kept constantly. v = o for all negative values of x when t = o. The theory of differential equations of this type teaches us that if we can obtain any one solution for each of these equations that satisfies its boundary conditions it is the only solution. The following are unique solutions of (5) and (6) subject to these conditions :

$$u = \frac{2U_0}{\sqrt{\pi}} \int_{\frac{2a}{i}}^{\infty} e^{-\beta^2} d\beta^3, \qquad (7)$$

$$v = \frac{V_0}{\sqrt{\pi}} \int_{-\frac{x}{2b^{+}\tilde{t}}}^{x} e^{-\beta^{*}} d\beta, \qquad (8)$$

in which  $\beta$  is merely a variable of integration. These may be seen to be solutions of (5) and (6) respectively if we differentiate them according to the rules for the differentiation of a definite integral and substitute the results in (5) and (6). Equation (7) is also seen to satisfy the initial conditions, for if t = 0 and x is positive the lower limit of integration becomes  $\infty$  which is the same as the upper limit; the integral is therefore 0 and u = 0. If x = 0 the lower limit is 0 and the value of the integral is  $\sqrt{\pi}/2$ 

$$\therefore u = U_0$$

Similar reasoning shows equation (8) to satisfy initial conditions for v.

The *metastable product H*, as we have defined it on page 8 (eq. 2), should be given by the following equation:

$$H = u^{2}v = \frac{4U_{0}^{2}V_{0}}{\pi^{\frac{3}{2}}} \left[ \int_{\frac{x}{2a^{V_{t}}}}^{\infty} e^{-\beta^{2}} d_{j} \right]^{2} \cdot \int_{\frac{x}{2b^{V_{t}}}}^{\infty} e^{-\beta^{2}} d_{j} \beta.$$
(9)

It is our problem to ascertain whether H is a constant for several initial concentrations of  $U_0$  and  $V_0$ .

If we knew the diffusion constants  $a^2$  and  $b^2$  we could expand the integrals in (7) and (8), integrate term by term for a given value of x and t, and thus obtained u and v and from them H. This would necessitate a previous independent determination of the diffusion constants, and would beside be very laborious, as the series do not begin to converge until after the sixth or seventh term. The difficulty of the series expansion might, however, be obviated by the employment of tables that have been computed for the definite integral.

easy deduction from equation (9). In order for H to be a constant the lower limits of integration

$$\frac{x}{2a\sqrt{t}}$$
 and  $\frac{-x}{2b\sqrt{t}}$ 

should be constant for all rings in a given tube with given initial values of  $U_0$  and  $V_0$ , and since *a* and *b* are constants,  $x/\sqrt{t}$  should be a constant. That is, for example, if we plunge a tube containing potassium chromate in gelatine into a solution of silver nitrate and observe with a cathetometer the distance from the bottom of the tube at which each thin disc of precipitate appears, and note, at the same time, the number of seconds that have elapsed since plunging in the tube, the distance divided by the square root of the time is a constant for all the discs in this tube, and for all tubes with the same initial concentrations of the reacting substances. The following sample set of results, Table II., and all the Tables IV. to XXIV., pages 147-150, show with what consistency this conclusion is verified.

/ sec.	<i>x</i> cm.	x   Jt.	f sec.	<i>x</i> cm.	x 1.
1245	.537	.01522	3823	.940	.01520
1420	.575	.01526	4305	.998	.01521
1607	.611	.01524	4842	1.056	.01518
1825	.649	.01519	5443	1.125	.01524
2068	.694	.01526	6102	1.188	.01520
2345	.738	.01524	6870	1.260	.01520
2658	.785	.01523			.01523
3000	.834	.01523		Mean Error,	.00002
3395	.888	.01524		,	

Temp. 15.7.	Silver Nitrate N.	Potassium	Chromate N	/75.

TABLE II.

III. DETERMINATION OF THE DIFFUSION CONSTANT AND THE METASTABLE LIMIT.

This constancy of x/1 t for any one set of observations under given conditions does not show, when taken alone, that there is a constant metastable solubility product H, but does show that, for a

given concentration of one of the ions, there is a definite concentration of the other ion that will cause precipitation.

In order to examine into the consistency of H, the product of ionic concentrations as defined by equation (9), we shall need to employ the data furnished by different initial concentrations of the reacting substances, as collected in the adjacent table (III.).

### TABLE III.

Recapitulation from Tables IV.-XXIV. Silver nitrate 2N diffusing into (a) Potassium Chromate N[75.

Table.	Temp.	x/ 1 7.
IV.	16.0	.01656
v.	16.3	.01663
VI.	16.3	.01671
VII.	16.1	.01700
Mean,		.01670

(b) Potas	sium Chroma	te N <b>75</b> .	(d) Potas	sium Chromat	e N/150.
Table.	Temp.	x/2t.	Table.	Temp.	x/1.
II.	15.7	.01523	XI.	17.3	.01462
VIII.	15.5	.01524	XII.	16.3	.01466
IX.	17.0	.01549	XIII.	16.7	.01467
Х.	16.7	.01533	XIV.	16.5	.01462
Mean,		.01530	XV.	15.5	.01453
,		101300	XVI.	16.6	.01477
			XVII.	16.6	.01468
			Mean,		.01465

Silver	Nitrate	NI2	diffusing	int
Suver	ivitraie	1814	ain <b>H</b> sinp	inic

(c) Potassium Chromate N/75.			(e) Potassium Chromate N/150.		
Table.	Temp.	x/Jt.	Table.	Temp.	x! Nt.
XVIII.	16.6	.01384	XX.	17.7	.01311
XIX.	16.8	.01377	XXI.	16.9	.01292
	Mean.	.01380	XXII.	16.0	.01335
	,,	101000	XXIII.	15.5	.01313
			XXIV.	15.5	.01299
			Mean,		.01310

diffusion constant  $a^2$  and the value of H, as defined by equation (9). For example, if we substitute for  $U_0$ ,  $V_0$  and  $z/\sqrt{t}$  the respective values of these quantities in sections (a) and (b) of Table III., we obtain the following equations:

$$H = \frac{4 \cdot 2^2 \cdot \frac{1}{75}}{\pi^{\frac{3}{2}}} \left[ \int_{\frac{.0167}{2a}}^{\infty} e^{-\beta^2} d\beta \right]^2 \cdot \int_{-\frac{.0167}{2b}}^{\infty} e^{-\beta^2} d\beta$$
(10)

$$H = \frac{4 \cdot \frac{1^2 \cdot \frac{1}{7_{-5}}}{\pi^{\frac{1}{2}}} \left[ \int_{\frac{.0153}{2a}}^{\infty} e^{-\beta^2} d_i \beta \right]^2 \cdot \int_{-\frac{.0153}{2b}}^{\infty} e^{-\beta^2} d_i \beta.$$
(11)

These two equations must be solved as simultaneous. We have been able to do this by the aid of a set of definite integrals given in the appendix of Kramp's *Analyse des Réfractions Astronomiques et Terrestres*, published at Strassburg in 1799. Kramp's table contains values of the integral

$$\int_a^\infty e^{-\beta^2} d\beta$$

for 301 values of  $\alpha$  from 0 to 3.00. This table shows, in the first place, that various values of

$$\int_{-\frac{x}{2b}}^{\infty} e^{-\beta^2} d \beta^2$$

obtained on the assumption that  $b^2$  is of the order of magnitude of the diffusion constant of an electrolyte and that  $x/\sqrt{t}$  is of the order of magnitude given by our experimental data, differ from each other and from  $\sqrt{\pi}$  by less than 2 per cent. This means merely that the change of concentration, v, of the substance originally in the gelatine can be neglected.

Dividing equation (11) by equation (10) and extracting the square root we have:

$$\int_{\frac{100}{2a}}^{\infty} e^{-\beta^2} d_i^{\beta} = 2.$$
(12)

To solve this equation for a it is only necessary to find two values in Kramp's table for which the lower limits of integration are in the ratio 0.0167 to 0.0153 and for which the value of the integral corresponding to the second is double the value of the integral corresponding to the first.

To give an idea of the procedure in such a calculation we shall give a few values from Kramp's table in the neighborhood of the solution, of which the starred value is seen to be the one satisfying equation (12).

The ratio of 0.0167 to 0.0153 is 1.091.

 $\alpha$  and  $\alpha_1$  are the lower limits of integration, A and  $A_1$  the corresponding values of the integral. The correct solution is singled out by the relation  $A/A_1 = 2$ .

a	a,	a_1/a	A	A <sub>1</sub>	A'A1
1. <b>77</b>	1.932	1.091	.010909	.005677	1.921
1.79	1.954	**	.010067	.005077	1.983
• 1.80	1.965	**	.009668	.004837	1.999
1.81	1.975	**	.009284	.004632	2.005
1.83	1.999	**	.008555	.004164	2.055

From which the value of  $\alpha$  that most nearly satisfies equation (12) is seen to be 1.80.

$$\therefore \frac{.0153}{2a} = 1.80,$$

$$a = 4.25 \times 10^{-3}$$

The corresponding value A of the integral is .009668. Therefore from equation (11)

$$H = \frac{4}{75\pi} (.009668)^2$$
  
= 1.6 × 10<sup>-6</sup> (  $\frac{\text{gm. mol.}}{\text{liter}}$ )<sup>3</sup>.

The diffusion constant is not a, but  $a^2$ , which reduced to the usual units with the day as unit of time by multiplying  $a^2$  by  $8.64 \times 10^4$  becomes

$$a^2 = 1.56 \; (\mathrm{cm}^2/\mathrm{day}).$$

In this calculation of H the reacting substances have been assumed to be completely dissociated. The result of the calculation shows that the concentration of the silver ion was about 1/200 normal and that of the chromate ion 1/75 normal when precipitation occurred. The dissociation of N/200 silver nitrate differs so little from that of N/400 which enters into the calculation of subsequent cases that the assumption of its complete dissociation introduces no appreciable inaccuracy. On the other hand the dissociation of N/150potassium chromate is about 1.05 times the dissociation of N/75, and this factor representing the ratio of dissociation must be introduced into calculations involving different concentrations of potassium chromate in the gelatine.

Observing this precaution we obtain the following values for  $a^2$  and H from other sets of data of Table III.

Results.
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For the Diffusion Constant of Silver Nitrate and the Metastable Solubility Product of Silver Chromate in Gelatine at 16° C.

From Table III. Data.	Diffusion Constant. cm <sup>2</sup> /Day.	$ \begin{pmatrix} Metastable Product \\ G. Mol \\ Liter \end{pmatrix}^{3} $
(a) and $(b)$	1.56	1.6 × 10-6
(b) and $(c)$	1.56	$1.6 imes10^{-6}$
(a) and $(c)$	1.56	1.4 × 10−⁵
(d) and $(e)$	1.53	1.3 × 10-6
(b) and $(d)$	1.50	$1.1 \times 10^{-6}$
(c) and $(e)$	1.53	1.3 × 10-6
Mean.	1.54	1.4 × 10-6

#### IV. DISCUSSION OF RESULTS.

The values obtained for the diffusion constant and for the metastable solubility product are constant within the limit of error of the method, as will be seen by a reference to the recapitulation of Table III. While the value of  $x/\sqrt{t}$  for any particular tube is constant within one or two tenths of one per cent. the same good agreement is not obtained when several series of observations are made upon different tubes under as nearly as possible the same conditions. The mean deviation of different tubes from the average is as great as one per cent. We think this deviation can be accounted for by lack of uniformity in the bore of some of the tubes, so that the diffusion takes place in a conical cavity instead of in a truly cylindrical cavity as the theory requires. That an error of one per cent. in the determination of  $x/\sqrt{t}$  will account for the variations in the values of  $a^2$  and H may be seen by a glance at the result of a recalculation of these quantities from the data (d) and (e) of Table III., on the assumption that the correct value of  $x/\sqrt{t}$  in (e) is .0130 instead of .0131;  $a^2$  comes out to be 1.63 cm.<sup>2</sup>/ day and H becomes 1.9 × 10<sup>-6</sup>. Or assuming  $x/\sqrt{t}$  to be .0132 instead of .0131,  $a^2$  becomes 1.42 and H becomes 0.7 × 10<sup>-6</sup>.

In view of this sensitive dependence of the diffusion constant and the metastable product on the value of  $x/\sqrt{t}$ , we consider the results to be satisfactorily consistent.

We have not been able to find elsewhere any determination of the value of the diffusion constant of silver nitrate in gelatine. F. Voigtlaender<sup>1</sup> has found that the diffusion constants of salts in agar from his own measurements are in some cases smaller, in others equal to or larger than the corresponding constants for water solutions, the solutions employed having varying concentrations. He says that the question whether the diffusion in agar and water is identical can only be answered by further observations on pure water and other gelatinous solvents, such as water glass. Voigtlaender's measurements point to the conclusion, however, that the diffusion in agar and that in water are not very different, which makes our result for silver nitrate, 1.54, seem rather high, as the values obtained by Kawalki<sup>2</sup> would be for silver nitrate at 16° C. 1.13 to 1.20. Calculation of the diffusion constant for silver nitrate by Nernst's formula

$$a^{2} = 0.0477 \times 10^{7} \frac{uv}{u + v} \left[ 1 + .0034 \left( t^{\circ} - 18 \right) \right]$$

gives the value 1.29.

It should be noted that the value we have obtained is for diffusion through gelatine containing a rather heavy solid precipitate of silver chromate, and should not, therefore, be expected to agree with diffusion in water or pure gelatine. The important fact for this dissistency in the conclusion that the metastable solubility product of silver chromate in gelatine is a definite constant quantity satisfying the relation

$$H = Ag^2 \times CrO_4.$$

As to the value of H, there are no other determinations of this quantity with which we might compare our results. As far as we know there have not been published any numerical data as to the value of the metastable product in any case. The ordinary solubility product of silver chromate in saturated water solution in the presence of the solid phase is  $5.1 \times 10^{-13}$  as determined by Kohlrausch.<sup>1</sup> The concentrations of  $Ag_2CrO_4$  in the two cases are in the ratio  $\sqrt[3]{1.4 \times 10^{-6}}/\sqrt[3]{5.1 \times 10^{-13}}$ . This means that the supersaturated gelatine at the concentration of precipitation held in solution 145 times the amount of silver chromate required to saturate it in the presence of the solid phase.

Lobry de Bruyn<sup>2</sup> and Liesegang<sup>3</sup> have shown that in the case of a large number of substances, which, like the silver haloids, form amorphous precipitates, gelatine inhibits precipitation. This phenomenon is especially easy to observe and demonstrate in the case of colored substances like silver chromate and lead iodide. It is well known that electrolytes whether or not they act chemically on the colloid may cause the precipitation of a colloid from solution, and it might be supposed that the case we are discussing can be explained as such an action of the diffusing silver nitrate in throwing down colloidal silver chromate. We are of the opinion that this is not the case, because, first, precipitation is here sudden and not slow, as is the case when colloids are precipitated by electrolytes, and second, in the several cases of different concentrations of the reacting substances, the precipitate is formed, not for a constant concentration of the diffusing electrolyte, but for a constant value of the product

 $A\bar{g}^2 \times Cr\bar{O}_4$ .

#### No. 3.] SUPERSATURATION IN GELATINE.

carbonates, both of which form insoluble compounds with silver. Although the silver salts of these radicals are more soluble than silver chromate it was thought necessary to remove them and other salts as thoroughly as possible from the gelatine to avoid their possible influence on the precipitation of the silver chromate. This removal was effected by electrolyzing the gelatine between membranes of parchment paper at 500 volts continually for a week, during which time the membranes and electrodes were frequently washed by a stream of distilled water. Specimens of gelatine so prepared gave but a trace of ash on ignition.

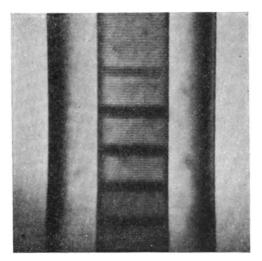


Fig. 4. Precipitation in commercial gelatine showing fine white lincs between the heavy dark deposits of  $Ag_2CrO_4$ . This is a section of a tube like Fig. 2, magnified 10 diameters.

Liesegang in his original research on reactions in gelatine solutions in capillary tubes found two classes of rings; the heavy widely separated red deposits of silver chromate, and beyond these and between them another series consisting of fine, microscopic white lines. According to Liesegang's description when the time came for the formation of a new red line one of the fine white lines suddenly became yellow and grew broader until it encompassed four of the white lines and developed into the dark red of silver chromate. Liesegang observed, however, that these white lines are not

necessary for the formation of the'red ones and are not present when chromate diffuses into gelatine impregnated with silver. We are of the opinion that these secondary white lines are due to the presence of impurities in the gelatine, since they appear with the same distinctness when silver nitrate diffuses into commercial gelatine to which nothing has been added. They did not appear in our purest electrolyzed gelatine. The addition of soluble chlorides, bromides or iodides in very small quantities causes the white rings to appear. Figs. 4 and 5 shows them between the larger lines of silver chromate. It is our intention to investigate further the possible influence of impurities on the formation of these precipitates.

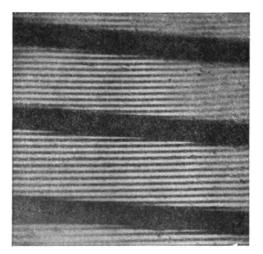


Fig. 5. Section of a plate like Fig. 1, magnified 20 times, showing two sets of rings in commercial gelatine.

It is of interest to know that gelatine is not necessary for the production of rings, for when a very fine capillary tube filled with a *water solution* of potassium chromate is carefully plunged into a silver nitrate solution precisely similar phenomena may be observed. In this case, however, the layer of precipitate exists for only a short time after its formation. It breaks up under the influence of gravity and convection and mingles with the mass of silver chromate below. Three or four layers may exist at the same time, those of later formation being sharp, and the older ones gradually disintegrating into a mass of precipitate.

### V. CONCLUSION.

We have shown by quantitative measurement that there exists in the case of the formation of silver chromate in gelatine solution a definite constant product

$$Ag^2 \times CrO_4 = H$$
,

which determines the limit of supersaturation with respect to silver chromate in the absence of the solid phase.

Incidentally we have obtained a value for the diffusion constant of silver nitrate diffusing through gelatine containing solid silver chromate.

TABLE IV.				TABLE VI.	•
remp. 16.0. Silver Nitrate 2N. Potas- sium Chromate N/75.		Temp. 16.3. Silver Nitrate 2N. Pola. sium Chromate N <sub>1</sub> 75.			
t sec.	<i>x</i> cm.	x'\$1.	t sec.	<i>x</i> cm.	x 11.
1732	.687	.01650	1705	.684	.01657
1920	.723	.01650	1885	.719	.01655
2350	.801	.01652	2083	.760	.01662
2596	.845	.01659	2300	.798	.01665
2865	.888	.01659	2540	.842	.01671
3170	.934	.01659	3090	.930	.01673
3505	.982	.01659	3405	.976	.01763
3870	1.032	.01662	3740	1.023	.01673
4315	1.083	.01652	4110	1.077	.01680
4900	1.139	.01662	4525	1.128	.01679
		.01656		-	.01671

TABLE V.

Temp. 16.3. Silver Nitrate 2N. Potassium Chromate N/75.

1 .1222.2.2

TABLE VII.

Temp. 16.1. Silver Nitrate 2N. Potassium Chromate NI75.

	-	Totassium Chromate 10/15			<i>w</i> // <b>5</b> .
t sec.	<i>x</i> cm.	x   11.	/ sec.	.r cm.	x/Jl.
1625	.672	.01667		_	
1805	.705	.01660	1580	.674	.01696
2000	.742	.01660	1750	.711	.01700
2215	.782	.01662	1940	.747	.01694
2450	.822	.01661	2150	.788	.01700
2710	.866	.01663	2385	.830	.01700
2995	.910	.01663	2625	.870	.01702
3300	.955	.01663	2910	.920	.01703
3645	1.003	.01662	3215	.963	.01699
4020	1.005	.01658	3550	1.015	.01704
4020 4430	1.107	.01663	3920	1.065	.01701
		.01663	4320	1.117	.01700
4885	1.162		4755	1.171	.01699
5365	1.220	.01666	4755	4.4/4	
58 <b>95</b>	1.280	.01667		1	.01700
		.01663		-	

No. 3.]



## TABLE VIII.

### TABLE XI.

siun	n Chromate N	75.	sium	Chromate N	150.
t sec.	x cm.	x'^t.	t sec.	.x cm.	x ~!t.
1530	.598	.01529	1332	.529	.01450
1745	.638	.01527	1535	.575	.01468
1 <b>985</b>	.680	.01526	1790	.619	.01460
2564	.771	.01523	2090	.670	.0146
2903	.819	.01521	2422	.721	.01465
3290	.872	.01521	2830	.780	.01466
3720	. <b>9</b> 27	.01521	3280	.838	.01463
4210	.986	.01524		1	
		.01524			.01462

# TABLE IX.

•	Temp. 16.7. Silver Nitrate N. Po sium Chromate N/75.		
t sec.	x cm.	xivt.	
1440	.585	.01535	
1605	.619	.01545	
1795	.655	.01546	
2010	.695	.01551	
2240	.734	.01551	
2785	.819	.01551	
3450	.911	.01551	
3845	.964	.01555	
		.01549	

# TABLE X.

sec.	x cm.	x Vt.
1073	.498	.01520
1165	.523	.01532
270	.546	.01532
1500	.594	.01534
635	.622	.01538
.778	.649	.01538
1935	.675	.01535
2105	.706	.01539

# TABLE XII.

#### Temp. 16.3. Silver Nitrate N. Potassium Chromate N/150.

f sec.	<i>x</i> cm.	x . t.
800	.413	.01461
920	.443	.01461
1050	.473	.01459
1215	.508	.01456
1400	.548	.01465
1605	.586	.01463
1850	.631	.01466
2120	.675	.01466
2425	.724	.01470
2780	.775	.01470
3180	.830	.01471
3633	.884	.01466
4130	.949	.01475
4710	1.013	.01474
	: .	.01466



	CABLE XII			TABLE XVI	
mp. 16.7. sium	Silver Nitra Chromate N	te N. Potas- 150.	Temp. 16.6. siun	Silver Nitral n Chromate N	
t sec.	<i>x</i> cm.	$x/\sqrt{t}$ .	/ sec.	<i>x</i> cm.	x' 1.
1270	.520	.01459	945	.453	.01474
1465	.557	.01454	1090	.485	.01469
1685	.602	.01466	1260	.535	.01479
1935	.645	.01466	1460	.564	.01476
2225	.694	.01471	1685	.608	.01481
2555	.743	.01470	1950	.654	.01481
2910	.794	.01471	2250	.702	.01478
3345	.847	.01465	2605	.756	.01481
3810	.908	.01471	2995	.809	.01478
4340	.970	.01472	3440	.867	.01478
		.01467			.01477
]	TABLE XIV	7.	1	ABLE XVI	I.
mp. 16.5. siun	Silver Nitra n Chromate N		Temp. 16.6.	Silver Nitra n Chromate N	te N. Pot
/ sec.	<i>x</i> cm.	x 1 1 2.	t sec.	<i>x</i> cm.	x!~!t.
1225	.511	.01460	1080	.479	.01458
1410	.551	.01468	1245	.515	.01462
1653	.595	.01464	1425	.554	.01468
1930	.644	.01466	1630	.592	.01466
2243	.692	.01461	1865	.637	.01475
2606	.746	.01461	2130	.679	.01467
3028	.803	.01460	2460	.728	.01468
3500	.862	.01457	2790	.780	.01477
		.01462	3170	.833	.01479
=	Table XV	=	10050	1.467	.01463
mp. 15.5.	Silver Nitra			1	.01468
siun	n Chromate N	150.	Т	ABLE XVII	т
/ sec.	<i>x</i> cm.	x 1 1.	Temp. 16.6.	Silver Nitrate	N/2. Pot
965	.451	.01452	siu	m Chromate N	75.
1108	.484	.01454	f sec.	<i>x</i> cm.	x vt.
1295	.526	.01462			x:~1.
1505	.564	.01454	905	.421	.01399
1745	.609	.01458	1105	.461	.01387
2025	.654	.01453	1210	.485	.01394
2345	.703	.01452	1333	.506	.01386
2702	.755	.01453	1468	.530	.01384
3115	.811	.01453	1765	.586	.01395
3595	.872	.01455	1935	.606	.01378
4165	.937	.01452	2120	.636	.01382
4770	1.002	.01451	2316	.661	.01374
5500	1.077	.01452	1543	.693	.01374
6280	1 166	01449	2780	726	01377

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#### TABLE XIX.

Temp. 16.8. Silver Nitrate N/2. Potassium Chromate N/75.

t sec.	<i>x</i> cm.	x/~1.
1625	.555	.01377
1870	.596	.01378
2145	.640	.01382
2460	.683	.01376
2820	.734	.01382
3294	.784	.01366
3705	.839	.01379
		.01377

# TABLE XX.

Temp. 17.7. Silver Nitrate N/2. Potassium Chromate N/150.

f sec.	<i>x</i> cm.	x/2t.
1026	.420	.01311
1244	.460	.01304
1510	.508	.01307
1819	.558	.01308
2181	.614	.01315
2625	.672	.01312
3185	.740	.01311
3850	.819	.01320
4700	.901	.01314
5720	.988	.01307
		.01311

#### TABLE XXII.

Temp. 16.0. Silver Nitrate N/2. Potassium Chromate N/150.

f sec.	.x cm.	x/ 1.
1305	.484	.01340
1560	.529	.01340
1880	.580	.01337
2270	.633	.01329
2730	.697	.01334
3270	.761	.01331
		.01335

#### TABLE XXIII.

Temp. 15.5. Silver Nitrate N/2. Potassium Chromate N/150.

t sec.	<i>x</i> cm.	$x \sqrt{t}$ .
933	.400	.01310
1120	.440	.01315
1340	.481	.01314
1590	.525	.01317
1900	.572	.01312
2265	.625	.01310
2690	.681	.01313
3190	.742	.01314
		.01313

# Table XXI.

Temp. 16.9. Silver Nitrate N/2. Potassium Chromate N/150.

t sec.	<i>x</i> cm.	x/~t.
705	,346	.01274
860	.380	.01296
1048	.419	.01294
1282	.465	.01298
1535	.508	.01297
1862	.559	.01295
2250	.614	.01295
2715	.674	.01293
3250	.734	.01288
		.01292

# TABLE XXIV.

Temp. 15.5. Silver Nitrate N/2. Potassium Chromate N/150.

/ sec.	<i>x</i> cm.	x!~t.
900	.387	.01290
1080	.427	.01299
1300	.465	.01290
1565	.513	.01297
1875	.564	.01303
2235	.615	.01301
2670	.674	.01305
3180	.738	.01306
		.01299

#### THE HYPOTHESES OF COLOR VISION.<sup>1</sup>

#### BY FRANK ALLEN.

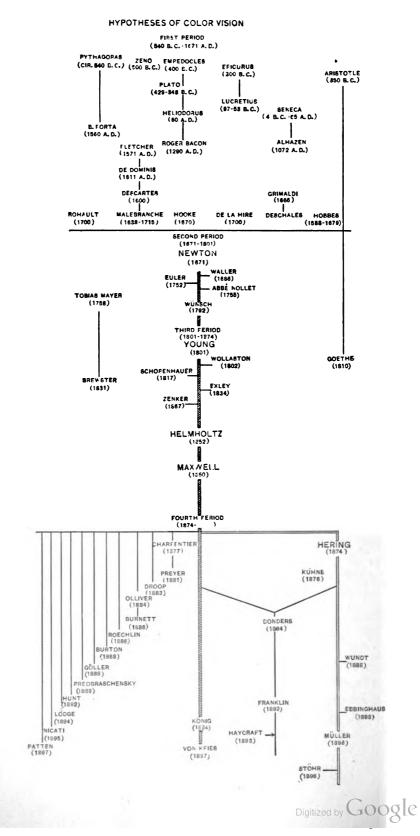
TO the question "How do we see?" there are but two general replies, the eye must emit something, or something from without must enter the eye. For twenty centuries this was a debated question among philosophers who took sides with the leaders of their respective schools, and vigorously upheld their theories. A complete absence of experiment in this as in other branches of science was accompanied by an astonishingly great variety of arguments and extravagant hypotheses to support their adopted opinions. Colors were ranked among the bodies of which only the names were known. When philosophers were asked, for example, why such a body was red, they answered that it was in virtue of a quality which made it appear red.

It is far from obvious that white light is very complex in its nature; and failure to discover this resulted in the confusion of mind exhibited by writers on light and colors preceding Newton's decisive experiments.

In the following short sketch of the history of this interesting branch of science an attempt is made to outline briefly most of the hypotheses of both ancient and modern writers. An outline only is attempted because a full review would expand this paper into a volume.

For the present purposes the history of color vision is here divided into four periods: first, from Pythagoras to Newton (540 B. C.– 1671 A. D.); second, from Newton to Thomas Young (1671–1801); third, from Young to Ewald Hering (1801–1874); fourth, from this last date to the present time.

FIRST PERIOD (540 B. C.-1671 A. D.).



vision is caused by particles continually flying from the surfaces of bodies and entering the eye.

A century after these, Empedocles and Plato put forward the doctrine that the cause of vision is something emitted by the eye which meeting with something else that proceeds from the object is thereby reflected back again. In other words sight was considered a species of touch due to invisible feelers having their origin in the eye.

Aristotle (De Anima, Lib. 2, Cap. 6: 350 B. C.) maintained that light is incorporeal. His ideas are best illustrated by a reference to the rainbow, in accounting for which very many theories of color production originated. He thought that the colors were due to imperfect reflection from raindrops, the image of the sun being distorted and color only exhibited. Aristotle also taught that black and white were the colors from which all others were derived, an idea which in modified form persisted to the time of Goethe. It was also supposed by some philosophers of this period that the rainbow was caused by the clouds communicating their-color to the sunbeams.

Epicurus (300 B. C.) and after him Lucretius (75 B. C.) believed that we see by the intervention of light as we feel an object by means of a stick. Seneca, who flourished about 60 A. D., observed (Nat. Quest., Lib. 1, Cap. 7) that sunlight shining through an angular piece of glass gives the colors of the rainbow, which he explained as a species of false color such as is observed on the neck of a pigeon. His theory of the rainbow is interesting. "The rainbow must be circular of necessity just as waves spread in a circular manner from a disturbance in still water." Again, he says : "that the rainbow is the image of the sun reflected from a hollow moist cloud which distorts the image because of the nature and figure of the speculum. Since in water everything is seen larger, the image of the sun is large because it is reflected from a moist cloud which partakes of the nature both of glass and of water." The different colors are accounted for by supposing that they come partly from the sun, partly from the clouds, and form a mixture?

Heliodorus, a Stoic philosopher of Nero's time, adhered to the old theory of the emission of ocular beams, which he tried to strengthen by arguing from the shape of the eye.

Ptolemy, whose treatise on optics written about 150 A. D. is now lost, became the great authority on the subject to the time of Alhazen.

During the Dark Ages the Arabians were the scientific investigators. The treatises of two of them, Al Farabi and Ebu Haithem (about 1000 A. D.), are not now extant; but that of Alhazen, published about 1072, became the authority for the five succeeding centuries. His speculations on color do not however show any advance over those of European philosophers. He defines the colors of the rainbow to be three, but with Seneca supposes them to be produced by a mixture of sun's light with the blackness of the cloud from which it is reflected. In the same manner the colors of all bodies seen by reflection are tinged with the colors of the reflecting surface (Optica, p. 461). The colors due to refraction in a glass globe, he says, are not the same as those of the rainbow, because they are not of the same number and are not seen in the same way — by reflection — but by direct vision in the same manner as light itself.

Roger Bacon, who died in 1294 A. D., assented to the opinion of some of the ancients and of some of his contemporaries as well, that visual rays proceed from the eye. His great reason was that everything in nature is qualified to discharge its proper functions by its own powers in the same manner as the sun and other celestial bodies. He regarded the presence of light necessary for vision (Opus Majus, p. 289).

Johannes Baptista Porta, who published his work, "Magia Naturalis," in 1560 when but fifteen years old, performed experiments with the camera obscura, invented by himself at that time, which convinced him that vision was caused by the intromission of light into the eye. Light was considered by him to be colorless but capable of having color superinduced upon it from foreign causes. He also gives an account of the generation of each color of the rainbow from a mixture of light and the denser or rarer parts of the air. Later Porta expressed the opinion that the colors of the rainbow were produced by refraction in the whole body of rain or vapor and not in the separate drops (De refractione, p. 95).

Fletcher, of Breslau (1571), tried to account for the colors of the rainbow by means of two refractions in one drop and a reflection

#### No. 3.] THE HYPOTHESES OF COLOR VISION.

from a second, but as is well known, Antonio De Dominis, Bishop of Spalatro (1611) arrived at the true explanation (De radiis visus et lucis).

To account for the color he supposed that the red rays were those that had traversed the least space inside the drop and accordingly retained most of their native force, and striking the eye more vigorously gave it a stronger sensation. Similarly green and blue were produced by those rays, the force of which had been in some measure lessened in passing through a greater body of water. All the intermediate colors were composed of mixtures of these three primaries according to the hypothesis which generally prevailed at the time.

The theory of De Dominis was adopted and mathematically investigated by Descartes (1596-1650). But while sound in his investigations of the paths of the rays, he was much less happy in the way he accounted for the production of colors. "Light is neither a substance nor yet a mere property of bodies, but the motion of a subtle fluid communicated by the pressure of a luminous body. It is affected by two motions, a circular and a direct. When the circular is quicker than the direct the color is red; if the direct is quicker the color is blue; when the motions are equal the color is yellow. All the other colors are composed of these primaries." Descartes was, however, the first to state the real nature of black and white.

Malebranche (1638–1715) modified this theory of Descartes by the substitution of a medium filled with fluid vortices instead of perfectly elastic solid globules.

Following the example of other philosophers, Thomas Hobbes (1588–1679), an English writer, published a theory based upon experiments with a prism. The colored rays he considered to be due to modified light which he divided into two parts and named "first" and "second" light. The following extracts (English Works, vol. 1, p. 459; Molesworth Edition) will give an idea of his hypothesis. "Colour is light, but troubled light, namely such

FRANK ALLEN.

weak but first light passeth through a more resisting diaphanous body as glass, the beams which fall upon it transversely make redness: when the same first light is stronger the transparent beams make yellowness. When the second light is strong green is produced, but when weaker it generates purple.

"Whiteness is light, but light perturbed by the reflections of many beams of light coming to the eye together within a little space. Blackness is the privation of light."

Hobbes also considered that colors are formed from a mixture of white and black.

Perhaps the most extravagant opinion ever formed upon the subject of color vision was that of Dr. Hooke the contemporary and rival of Newton. Hooke reduced the primary colors from three to two. "Blue is an impression on the retina of an oblique and confused pulse of light whose weaker part precedes and whose stronger part follows; and red is a similar impression whose stronger part precedes and whose weaker follows. The fantasm of colour is caused by the sensation of the oblique or uneven pulse of light which is capable of no more varieties than two, which arise from the two sides of the oblique pulse though they be capable of infinite gradations, each of them beginning from white and ending, one of them in the deepest scarlet and the other in the deepest blue." (Priestley "On Vision, Light and Colours.")

De la Hire, who lived at this time, supposed difference in color to depend upon the degree with which the same light affects the optic nerve. For example, red blood appears blue through the veins because the light in passing through the skin loses its power and affects the nerve with less force. In common with many other writers he assigned the blue color of the sky to the sunlight reflected by the air, seen against a background of dark space.

Grimaldi (De lumine, coloribus et iride, 1666) made the discovery that when a circular beam of light passes through a prism it He concluded with Aristotle that light is no real substance; not a substantial but an accidental quality.

Priestley (On Vision, Light and Colours, p. 240) thus sums up the theories of color production to the time of Newton :

"The Pythagoreans called colour the superficies of a body. Plato said that it was a flame issuing from them. According to Zeno it is the first configuration of matter, and Aristotle said it was that which moved bodies actually transparent. Descartes very sensibly argued that colour is a modification of light; but he supposed that the difference of colour arises from the prevalence of the direct or rotatory motion of the particles of which it consists. Father Grimaldi, Deschales, and many others thought the differences of colour depended upon the condensation and rarefaction of light. Malebranche was of the opinion that differences in colour depend upon the quick or slow vibrations of a certain elastic medium filling the whole universe. Rohault imagined that the different colours were made by the rays of light entering the eye at different angles with respect to the optic axis; and from the phenomena of the rainbow he pretended to calculate the precise angle that constituted each particular colour. Lastly Dr. Hooke, the rival of Newton, imagined that colour is caused by the sensation of the oblique or uneven pulse of light; and this being capable of no more than two varieties, he concluded that there could be no more than two primary colours."

Note.— Most of the hypotheses comprising the First Period will be found in Priestley's "On Vision, Light and Colours."

Second Period (1671-1802).

1671. Newton. "New Theory of Light and Colours." Philo. Trans. (abridgment), Vol. I., p. 678. Reprinted in Pop. Sci. Monthly, Sept., 1902.

Newton performed his experiments on the decomposition of white light in 1666, but apparently did not publish the results until "To the same degree of refrangibility ever belongs the same colour, and to the same colour ever belongs the same degree of refrangibility."

"To explain colours I suppose that \* \* \* the rays of light by impinging on the stiff refracting superficies, excite vibrations in the ether \* \* \* of various bigness; the biggest, strongest or most potent rays, the largest vibrations; and others shorter according to their bigness, strength or power; and therefore the ends of the capillimenta of the optic nerve, which pave or face the retina, being such refracting superficies, when the rays impinge upon them, they must there excite these vibrations which \* \* \* will run along the aqueous pores or crystalline pith of the capillimenta through the optic nerve into the sensorium; and there, I suppose, affect the sense with various colours according to their bigness and mixture; the biggest with the strongest colours, reds and yellows, the least with the weakest, blues and violets; the middle with green; and a confusion of all with white \* \*."

1686. Waller : Phil. Trans., vol. 3, p. 274.

In this paper Waller describes the materials from which pigments of definite colors are made. He also briefly mentions experiments in which he mixed the simple red and yellow pigments with each of the simple blues, and concludes that these mixtures of primaries give most of the medium colors, namely, green, purple, etc.

1752. Euler: Nova theoria lucis et colorum. Lettres à une Princesse d'Allemagne, 1768. Nos. 23, 27 and 28.

Euler upheld the undulatory theory and strongly opposed the doctrine of light corpuscles. But he maintained that bodies became visible because the sun's rays fell upon them, throwing their particles into motion, generating in their turn rays which, affecting our eyes, rendered the bodies visible. The blue color of the sky he explained by supposing the dust suspended in the atmosphere to generate blue rays owing to their constituent particles being thrown into vibration by the sun's light.

1755. Abbé Nollet : Leçons de Physique, Tom. 5, Sec. 3. Quoted

by J. D. Forbes: Phil. Mag., S. 3, Vol. 34, p. 172, 1849. This writer taught the Newtonian theory of light and colors, but maintained the primary qualities of orange, green and purple.

#### **No. 3.**] THE HYPOTHESES OF COLOR VISION.

1758. Tobias Mayer: Gottingische gelehrte anzeigen, p. 147. Quoted by Helmholtz: Phil. Mag., S. 4, Vol. 4, p. 522, 1852.

The three colors, red, yellow and blue had been mixed as pigments in early times, and came to be regarded somewhat as primary colors. "Mayer was the first to give utterance to the view that the three primitive colours might correspond to three different kinds of light, red, yellow and blue, each of which furnished rays of all refrangibilities. According to this, at every point in the solar spectrum, red, yellow and blue rays are mixed together which do not differ in refrangibility and therefore cannot be separated by the prism."

1792. Chrétien Ernest Wünsch: Versuche und Beobachtungen über die Farben des Lichtes. Leipsic. Abstracted in Annals de Chimie, 64, p. 135, 1807.

Wünsch performed many experiments to prove that there were not seven primary colors as some supposed from the number of spectrum colors given by Newton, nor yet five as others believed. He was the first to select red, green and violet as primaries, a result to which he was led by his experiments on mixtures of the colored rays of the spectrum.

#### THIRD PERIOD (1801-1874).

1801. Thomas Young: "On Theory of Light and Colours." Phil. Trans., Vol. 92, p. 12, 1802 (read in 1801). "Some Cases of the Productions of Colours." Ibid., p. 387.

In the first paper Young selected red, yellow and blue as the three simple color sensations, with no other basis than current scientific opinion. Owing to the celebrated but misconstrued observations by Wollaston of the dark lines in the solar spectrum, Young modified his theory by selecting red, green and violet as primaries, quite independently, however, of Wünsch. This theory he further confirmed by experiments, after which it remained in obscurity until Maxwell and Hemholtz brought it to the attention of scientists and made it the basis of their investigations.

Young seems to have been the first to attribute a definite physiological significance to the three primary colors, the precise hues or

wave-lengths of which he had no means of determining. His general principles were modified and made definite by the experimental researches of Helmholtz, Maxwell, König and others. These do not all agree upon the hues selected as the primary colors, and Maxwell in particular selects a blue as the third of his triad of fundamentals.

"The referring of all colours," says Helmholtz, "to the three primitive ones has, in the case of the different observers, three different senses :

" I. That the different colours were such as permitted of the formation of all others from their combinations.

"2. Or, as supposed by Mayer and Brewster, that the primitive colours correspond to three different kinds of objective light.

"3. Or, as supposed by Young, that they correspond to three primitive modes of sensation experienced by the visual nerves, and from which the remaining sensations of colour are composed."

[Helmholtz : "On the Theory of Compound Colours." Phil. Mag., S. 4, Vol. 4, 1852, p. 522. Also "Physiol. Optik."]

- [Maxwell: "On Theory of Compound Colours, and the Relations of the Colours of the Spectrum." Phil. Trans., p. 57, 1860.] See also A. M. Mayer: "History of Young's Discovery of his Theory of Colors." Amer. Jour. of Science, Ser. 3, Vol. 9, p. 251, 1875.
- 1802. William Hyde Wollaston: "A method of examining refractive and dispersive powers by prismatic reflection." Phil. Trans., Vol. 92, p. 378.

In this paper Wollaston records his discovery of the principal "Fraunhofer" lines, the nature of which he was far from suspecting. He supposed that they divided the spectrum into four parts and formed the boundaries of the four corresponding colors, red, yellowish-green, blue and violet, the color of each division being quite uniform. He says that "we may distinguish, upon the whole, six species of rays into which a sunbeam is divisible by refraction." These are the four visible ones mentioned and in addition the invisible ultra-violet and infra-red. Wollaston evidently considered his four colors to be simple objective colored light.

This paper was important since it led Young to revise his theory.

# 1810. Goethe : "Farbenlehre." English translation, "Theory of Colours." Eastlake.

The hypothesis of Goethe is merely the absurd doctrine of the ancients that color is a mixture of light and darkness developed to a very high degree. "Light and darkness," Goethe says in the introduction to his work, "or light and its absence are necessary to the production of color." He bases his views on observations made by looking at a broad field of light (e. g., a window) through a prism, and draws the general conclusion that next to the light a color appears which is called yellow; another appears next to the darkness which we call blue. When these are mixed in equal proportions the resulting color is green. All these colors produce new tints by being mixed with darkness.

Goethe's writings on color are remarkable for the abuse and denunciaton which he heaped upon the experiments and color theory of Newton. To some of the propositions of Newton he applied such terms as "incredibly impudent," "mere twaddle," "ludicrous explanation," and others of a similar character.

1816. Schopenhauer: "Ueber das Sehen und die Farben." Abstract in Encyc. Brit., Vol. 21, p. 450.

"The distinction of white and black with their mean point in the gray is referred to the activity or inactivity of the total retina in the graduated presence or absence of full light. The eye is endowed with polarity by which its activity is divided into two parts qualitatively distinct. It is this circumstance that gives rise to phenomena of colour. All colours are complementary. Each pair makes up the whole activity of the retina and so is equivalent to white; and the two particular activities are so connected that when the first is exhausted the other spontaneously succeeds. Such pairs are infinite in number. But there are three pairs which stand out prominently and admit of easy expression for the ratio in which each contributes to the total action. Red and green (each equal to  $\frac{1}{2}$ ); orange and blue (2:1); yellow and violet (3:1).

1831. Brewster: On a New Analysis of Solar Light. Trans. Roy.
 Soc. Edin., Vol. 12, p. 123, 1834. (Read in 1831.)

Awarded the Keith Biennial Prize in 1834 by Roy. Soc. of Edin.

The theory of Brewster is an elaboration of that of Mayer based on observations of an *impure* spectrum. The main points of the theory are as follows:

I. Red, yellow and blue light exist at every point of the solar spectrum.

2. As certain proportions of red, yellow and blue lights constitute white, the color of every point of the spectrum may be considered as consisting of the predominating color at any point mixed with white light.

3. By absorbing the excess of any color at any point, white light appears at that point which cannot be decomposed by any number of refractions.

The great reputation of Brewster induced most physicists for more than twenty years to adopt this view, Airy, Melloni, Draper, and Helmholtz alone dissenting. This theory persists to the present time, and as Rood remarks, is almost universally believed by artists.

Helmholtz investigated the experiments which misled Brewster, and showed that he had employed a spectrum mixed with stray white light.

1834. Thomas Exley. "Physical Optics," p. 28.

The following condensed extract will give a general idea of the views of this writer :

"The atoms of light have equal velocities, but unequal momenta and spheres of repulsion; hence they ought to produce different effects or sensations on the delicate organ of vision. Probably those ethereal atoms which penetrate deepest into the sensitive part of the eye to produce their greatest effect give the red color, and those which pierce to the least depth produce violet, and those intermediate in proportion. Therefore the atoms which have the greatest absolute force and the least sphere of repulsion will cause a red color, and others according to one or other or to the proportion of both these circumstances will produce the same or other colors."

1867. W. Zenker. "Versuch einer Theorie der Farben perception." Archiv für Mikroskopische Anatomie (Schultze), Bd. 3, p. 248.

cones is supposed to have a greater refractive index than the layer Part of the light entering the eye is absorbed, and part reabove. flected, the latter being the portion of the radiant energy which excites the sensation of color. The elements of the retina may be considered as systems of surfaces upon which the incident lightwaves fall perpendicularly, and from which they are reflected in the same manner. These result in systems of standing waves with nodes at fixed distances from the reflecting layer, the distances depending upon the wave-lengths. The point of maximum disturbance will therefore be different for waves of different refrangibilities. The rods and cones, he says, are like piles of plates, each plate having a thickness equal to three standing waves of red, four of blue, and five of violet. The loops of the standing red waves will therefore always affect different plates from those acted upon by blue and violet, and hence these sensations will always be excited by the proper wave-lengths. This theory accordingly makes color perception a function of space not of time.

## FOURTH PERIOD (1874-).

1874. Ewald Hering. A series of six papers in: Sitzungs. der Kaiserl. Akad. der Wissen. zu Wien. (Math.-Naturwiss. Classe). Fifth paper: Grundzüge einer Theorie des Lichtsinnes. 69 (3), p. 179, 1874. Sixth paper: 70 (3), p. 169.

Papers collected under the title : Zur Lehre vom Licht-sinnes. Vienna, 1878.

The hypothesis of Hering, the great rival of the Young-Helmholtz theory, is based upon the idea of visual substances. Hering assumes six psychophysical processes corresponding to six primary sensations which may be arranged in complementary pairs, blackwhite, blue-yellow, green-red. Three photochemical substances are supposed to exist in the retina, one corresponding to each of the pairs of sensations. The sensations of white, yellow and red are caused by the dissimilation of the corresponding visual substances, and the sensations of black, blue and green are caused by the assimilation of the same substances. These substances are not present in equal amounts. All the rays of the visible spectrum have a dissimilating action on the black-white substance, but different rays in different degrees. Mixed light appears colorless when it acts on the blue-yellow or red-green substance with equal dissimilative and assimilative power. The effects are not complementary merely but antagonistic. For example, fundamental red and green do not produce white by their combination, but merely destroy each other's effect and leave visible the white which is already there. This is not strictly true of the white-black antagonism, for their actions do not destroy each other but give rise to a series of grays. Each visual sensation is really a mixture of all six fundamental sensations. The one of the six which has relatively the greatest weight gives the character and name to the mixed sensation.

1876. Kühne. Papers in : "Verhandlungen des Naturhistorische-Medicinischen Vereins zu Heidelberg," 1877–79.

Following close upon the discovery (1876) by Boll of the "Visual purple," Kühne constructed a theory of vision. He supposes that the waves of light give rise in the retina to different compounds according to their length, and thus produce the different color sensations.

1877. Augustin Charpentier. "De la vision avec les diverses parties de la rétine." Archives de Physiol., 4, p. 894; also, "Sur la distinction entre les sensations luminenses et les sensations chromatiques," Compt. Rend., 86, 1878, pp. 1272 and 1341. Theory further developed in numerous other short papers in Compt. Rend., e. g., 2 Semes, 1885, p. 275. Also see Nineteenth Century, August, 1893, Vol. 34, p. 258 in art. "Recent Science" by Kropotkin.

This theory distinguishes in optical phenomena : first, a luminous sensation; second, a chromatic sensation; third, a visual sensation, or a sensation of form. Charpentier supposes a double process chemical and thermal—of colored light upon two different pigments of the retina. The photochemical effect of light decomposes the visual purple and generates in the optic nerve one sort of vibrations totally independent of the color, and varying in amplitude with the intensity. Another pigment is supposed to be located between the rods and the cones which absorbs light and heat. This absorption generates in the nerve another set of thermal or thermo-electric undulations which always begin a little later than the former, the interval being greater for violet than for red.

Two waves are thus moving along the optic nerve with corresponding phases at different intervals. Their various combinations provoke a variety of sensations which we interpret as so many colors.

1881. W. Preyer: "Ueber den Farben- und Temperatursinn mit besonderer Rücksicht auf Farbenblindheit," Pflüger's Archiv, Bd. 25, p. 31.

In every color sensation Preyer distinguishes three parts : quantity or intensity; quality or tone; temperature. The intensity depends upon the force with which the retina is acted upon by the ether waves, the quality upon their amplitude. He also makes an æsthetic division of colors into two classes, warm and cold. The warm colors are from red to yellow green, the cold from this latter to violet. The color process is developed from an earlier existing temperature sense, and indeed the color sense may be considered a special case of the thermal sense limited to the retina. In this hypothesis, each retinal nerve fiber sensitive to color impressions terminates in two "cones," one of which is excited by warm colors and the other by cold, the deciding factor being the wave-length. The rods give sensations only of white, gray, and black, the cones the color sensations.

- 1882. E. Landolt : "Théorie de la perception des couleurs," Arch. d'Ophthalm., II., p. 79.
- 1883. H. R. Droop : "Colour Sensations," Phil. Mag., S. 5, 15, p. 373.

This very indefinite theory of color vision is based upon two cases of color blindness described by Holmgren. One of the persons saw only red and bluish green in the spectrum and was blind to blue and yellow; the other saw yellow and blue, but was blind to red and green. As these were cases of monocular color-blindness their observations were accurately described. From these data he out-

- 1884. A. Angelucci: "Una nuova teoria sulla visione," communic. preventiva presentata All' Acad. Med. de Roma, 14 July, 1884. Also in: Rec. d'Ophthalm., p. 34, 1886.
- 1884. F. C. Donders : "Noch einmal die Farbensysteme," Graefe's Archiv für Ophthalmologie, Bd. 30 (1), p. 15.

The theory of Donders comprises features of both the Young-Helmholtz and Hering theories, and at the same time introduces some new ideas of the possible mechanism of color perception; the most prominent being that of successive partial dissociation of the complex color molecules of a single visual substance, which gives rise to the four simple color sensations, red, yellow, green and blue. It is thus a four-color theory, but he supplemented this by a three color theory (red, green, violet) under certain conditions in order to obtain for his theory the advantages which a three-color theory has. 1884. C. A. Olliver. "A Correlation Theory of Colour Perception." Phila. Med. Times, 14, p. 715, 1883-4.

"Each and every healthy optic-nerve filament transmits to the color-center of the brain for recognition, nerve energies equal to as many special sensations as its peripheral tip is capable of perceiving. Color perception takes place through each and every optic nerve filament." Instead of separate nerves for several independent fundamental color sensations with the retina as the distinguishing factor, the "color-center" of the brain perceives color according to the specific energy transmitted.

1886. Roechlin.

The theory of this writer is that yellow and blue are the only two simple colors of the spectrum, the third being always found fused with yellow or blue to form reds and violets. Roechlin asserts that purple may be produced by combining violet and yellow, as well as by the mixture of red and blue.

1886. S. W. Burnett. "The new Theory of Color-perception." Amer. Jour. Ophthal., Vol. 3, p. 278.

1888. W. Wundt. "Die Empfindungen des Lichtes und der Farben." Philos. Studien, 4, p. 311.

Apart from every external light stimulation and from all equivalent internal stimuli such as pressure, the retina is in a constant condition of internal stimulation. To this corresponds the sensation black, which also in part accompanies the light stimuli giving rise to the sensation gray.

By means of every external retinal stimulation two different excitation processes are set free — a chromatic and an achromatic which follow different laws. With weak stimulation the achromatic has the greater intensity, with moderate light excitation the chromatic is more intense, while with the most intensive stimulation the achromatic is again predominant. The achromatic excitation consists in a *uniform* photochemical process which reaches its maximum in the yellow. The chromatic consists in a *polyform* photochemical process which represents a periodic function of the wave-length. Antagonistic action occurs not between the color stimuli themselves, but between the photochemical processes, and results in leaving a colorless light stimulus.

1888. Chas. V. Burton. "Experiments on Colour-perception, and on a Photo-Voltaic Theory of Vision." Cambridge Philos. Proc., Vol. 6, 1886-9, p. 308.

The author bases his theory upon experiments of Dewar and McKendrick (Edin. Philo. Trans., XXVII., 141), who have shown that there is a considerable electromotive force between the anterior portions of the eye and a transverse section of the optic nerve. It was found that the current flowing was altered in amount only when light fell upon the retina. Yellow and green rays produced the greatest effect. The converse phenomenon is well known that an electric current applied to the optic nerve produces a sensation of light.

The theory suggested is that electric currents in the nerve fibers produce the sensation of light, and, if of sufficient intensity, of color also. The light of all wave-lengths falling upon the retina affects these currents in various degrees which produce the phenomena of 1888. A. Göller. "Die Analyse der Lichtwellen durch das Auge." Dubois-Reymond's Archiv für Physiologie, I. and II., p. 139. Reviewed by C. L. Franklin: Am. Jour. Psych., Vol. 2, 1888-9, p. 155.

Göller explains the analysis by the eye of light waves into sensations of differently colored lights by rotatory polarization. "Monochromatic light, on entering the eye, passes through the transparent retina, and is reflected back from the pigment epithelium in a state of plane polarization. The outer members of the cones play the part of a plate of quartz - they shift the plane of polarization by a definite angle. A molecular motion of much slower period is then set up in the protoplasm of the inner members, and it is the sensitiveness of the nervous filament to the plane of this motion which constitutes the sensation of color. Two complementary colors are colors which have had their planes of polarization rotated, one ninety degrees more than the other, with a phase difference of a quarter wave-length, the amplitudes being the same. These conditions would be sufficient to cause their superimposed harmonic motions to produce the motion of circular polarization, and that would be indistinguishable from the motion produced by all the colors of white light acting together.

Two vibrations whose planes are at different angles would give an elliptic motion of such a kind that the direction of its major axis would give its tint, the excess of the major axis over the minor would give its saturation, and the minor axis would give the amount of white light mixed with it."

1889. Preobraschensky. "Hypothese des Farbensehens." Jour. Russ. Phys.-chem., phys. part. 21, p. 248. Abstract: Jour. de Phys., II., 9, 1890, p. 538.

In this article the author very seriously modifies the Young-Helmholtz theory. In place of three kinds of nerve elements he supposes two — one sensitive to waves from .400  $\mu$  to .600, the other to those between the wave-lengths .520 and .790. The simple sensations correspond to the extreme vibrations. The gray sensation is produced by the simultaneous impression of the same intensity of two colors equally distant from the extremes. The perception of the intensity of light is the same in both theories.

1892. C. L. Franklin. "Eine neue Theorie der Lichtempfindungen." Zeit. für Psych. und Physiol. der Sinnesorgane, 4, p. 211.
"On Theories of Light-Sensation." Mind, N. S., 2, 1893, p. 473.

"In the earliest stage of its development the visual sense consisted only in the sensation of gray, i. e., the whole black-graywhite series of sensations. There is a certain kind of molecule, called the 'gray-molecule' which is composed of an outer range of atoms somewhat loosely attached to a firmer inner core, and having different periods of vibration. The light waves of the entire spectrum in some measure, and particularly those of the middle part, have the power of tearing off this outer sheath of atoms which react chemically upon the retinal nerve ends, and bring about the sensation of gray. The color molecules are developed from the gray molecules in the following manner : The atoms of the outer range segregate themselves into three different groups at right angles to each other, and having three different average velocities. Light of the fundamental color tones (red, green and blue) tears off from a large number of molecules those atom groups whose periods are synchronous with the vibrations of the light, and those special chemical substances are set free which excite the respective color Intermediate waves set free atoms of two kinds and so sensations. give rise to mixtures of colors. Certain mixtures of light set free all three kinds of nerve-exciting substance which results in the gray sensation."

1892. Edmund Hunt: "Color Vision." Glasgow.

In a critical essay Hunt discusses several of the existing theories of color vision, and the interpretations of their experiments made by various writers. In addition he presents a theory of his own. Rejecting the various three-color and four-color theories, he maintains that there are five pure or principal colors : red, yellow, green, blue and purple. No attempt is made to describe any retinal processes by which the pure colors and their mixtures are perceived. Black and white are not considered as sensations.

<sup>1893.</sup> J. B. Haycraft : "A new Hypothesis concerning Vision." Proc. Roy Soc., 54, p. 272, 1893.

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This paper briefly outlines an evolutionary theory in which color perception is a development of an earlier existing light-sense. To be concrete, the sensation of yellow has in the course of evolution been produced by pigments which stimulate the eye by the yellow, red and green spectral rays which they transmit. The red and green rays when mixed do not, however, give rise to red and green sensations, but simply intensify the yellow sensations. In a similar way combinations of other rays are treated.

1893. H. Ebbinghaus: "Theorie des Farbensehens." Zeit. für Psych. u. Physiol. der Sinnes., 5, p. 145. Reviewed by C. L. Franklin. Mind, N. S., 3, p. 198, 1894.

This theory is a development of Hering's, with the distinctive idea-partial dissociation-of Donders. "The visual purple is identical with a photochemical substance of such a nature that its primary partial dissociation is the cause of the sensation of yellow, and its completed dissociation is the cause of the blue sensation. In the cones which contain no visual purple, that substance does in reality exist, but is concealed by the presence of a second visual substance which is successively green, red and white in color (i. e., is always complementary in objective color to the visual purple in all its color changes) and which is the source of our sensations of red and green. There is a third colorless substance in rods and cones alike whose decomposition is the source of the normal whitegray sensations, and of the sensations of the totally color-blind as well as of those of the normal eye when temporarily color-blind owing to insufficient illumination, besides contributing to the brightness of all sensations of light."

1894. Oliver J. Lodge. "The Work of Hertz." Nature, Vol. 50, p. 137.

In this review of Hertz's work a brief outline of an electrical theory of vision is given as follows: "I therefore wish to guess that some part of the retina is an electrical organ, say like that of conducting and the nerves are stimulated. This intervening layer acts as a coherer affected by Hertzian waves, or as selenium affected by ordinary light. The sensation of light is due to electrical stimulus; the sensation of black is due to the mechanical or tapping-back stimulus. Vision is persistent until this latter stimulus occurs. The energy of vision is supplied by the organism, the light only pulls a trigger."

1894. A. König. "Ueber den menschlichen Sehpurpur und seine Bedeutung für das Sehen." Sitz. Akad. Wiss. Berlin, Vol. II., p. 577.

In his papers König has developed the Young-Helmholtz theory along the line of assigning specific functions to the rods, cones, and visual purple. "He believes that the cones have nothing to do directly with the luminous sensation, but that they are catoptric instruments for the purpose of condensing light upon the walls of the pigment epithelium, where the photochemical processes take place which are the sources of the sensations of red, yellow and green. The blue sensation is furnished exclusively by the visual yellow of the rods, and the sensation of a faint light (and that of the totally color-blind) is also blue in quality and is due to the visual purple. Hence the fovea, where there is no visual purple, is blind to blue. The blue blindness of the fovea has not been confirmed by other observers."

1895. W. Nicati. "Théorie de la coleur." Archiv d'Ophthal., XI., p. 1. Reviewed by C. L. Franklin, Psychol. Rev., Vol. 3, 1896.

The author uses such words as protochroism, metachroism, pleochroism, for gray vision, partial color-blindness and normal vision respectively. There is no difference in rods and cones that will cause three-color sensations, but in the "bipolar cells" there is a separation of the terminations into three layers for the three sensations. The visual purple is chemically affected by light and generates electric currents which are conducted by threads of varying resistances. The strength of current which is conveyed by each thread determines the character of the color sensation. Suitable cells are provided near the threads which send down condenser

discharges to undo the effects of the first currents. For example, after red has been seen the discharge causes green.

1896. G. E. Müller. "Der psychophysischen Axiome und ihre Anwendung auf die Gesichtsempfindungen." Zeit. für Psychol. u. Physiol. des Sinnes., Bd. 10, 1896, p. 1. Second paper; *ibid.*, p. 321. Also two other papers, Bd. 14, 1897. Reviewed by C. L. Franklin: "Professor Müller's Theory of the Light Sense." Psychol. Rev., Vol. 6, 1899, p. 70.

The theory set forth in these lengthy papers is a modification of Hering's. Instead of the dissimilation and assimilation of visual substances as provided by Hering, Müller takes advantage of a conception of modern chemistry, namely the reversibility of chemical action under suitable conditions, which conditions, he assumes, are realized in the retinæ of vertebrate animals. The chemical law of mass action is also used in treating of the intensity of the photochemical processes. The pairs of sensations are the same as in Hering's theory except that a slight difference is made in the whiteblack process. Müller makes use of the "self light" of the retina in modifying the antagonism which exists between the black and white sensations. These do not naturally counteract each other perfectly, and so Müller assumes that the "self light" produces the gray effects. No use is made of the visual purple as a substance for producing vision, but it is regarded as an aid in bringing about adaptation to faint light.

1897. J. von Kries. "Ueber Farbensysteme." Zeitschrift f. Psych., XIII., p. 241. "Krit. Bemerk. zur Farbentheorie," *ibid.*, XIX., p. 175. 1898.

Von Kries in what has been termed a "reconstruction" of the Young-Helmholtz theory apparently inclines to the view "that there are two sorts of white — one physiological and brought about by a photochemical dissociation in the rods; the other psychical and due to a mental reconstitution of an even red-green-blue sensa-

#### No. 3.] THE HYPOTHESES OF COLOR VISION.

 1897. W. Patten. "A Basis for a Theory of Color Vision." Amer. Naturalist, 32, p. 833. Abstract : Science, N. S., 7, 1898, p. 219.

"The theory is based on the structure of retinal cells in invertebrates. The structures in the eyes of invertebrates corresponding to the rods and cones of vertebrates are generally composed of groups of simple or compound wedges, containing systems of transverse fibrils accurately graded in length, according to their positions in the wedges. The fibrils are always arranged in planes at right angles to the rays of light. All the fibrils in these planes may be parallel to one another, or at varying angles, or they may radiate from the axis of each rod like the bristles on a test-tube cleaner, so that no two fibrils in the same plane are parallel. By assuming that the length and angular relations of a fibril determine the amount of its response to a wave of light of a given length and plane of vibration, it is possible to offer a logical explanation of many phenomena of color vision."

1898. Adolph Stöhr. "Zur Hypothese der Sehstoffe und Grundfarben." Leipzig und Wien: Deuticke, 1898. Reviewed by C. L. Franklin: Psychol. Rev., Vol. 7, 1900, p. 415.

The author "assumes several visual substances, and also, in the end-apparatus of the optic nerve, ultra-microscopic visual elements or corpuscles which are excited, under proper conditions by the visual substances. It is further supposed that the direct action of light upon the visual corpuscles is already sufficient to set them into molecular vibration, and that the effect of the visual substance is simply to modify and to strengthen this vibration. The object of this duplex supposition is to combine in one a photo-chemical hypothesis and a photo-physical one. In the highest animals these substances are three in number, and they give rise to the elementary color sensations.

"The visual elements, corpuscles or threads as they are variously called consist of minute fibers each thickly strewn over its entire surface with projecting flat plates, four in a given plane, and composed of material of four different sorts fitted to respond to four different sorts of stimulus and to furnish three primary color sensations together with the sensation of white. The most characteristic part

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of the theory is that these little plates are set into molecular vibration in the first instance by the direct action of light (all alike in this case, and attended by the white sensation), but in the second instance this vibration is added to by the synchronous molecular vibrations of the three photo-chemical substances, when severally produced by light of different periodicity. It is then neither the production nor the destruction of a photo-chemical substance that is effective in exciting the nerve terminals, but it is during its relatively brief period of existence that a given substance acts upon the particular color-plate with which it is in harmony."

The various theories outlined in this paper are shown in their mutual relationship to some extent in the accompanying figure. From Newton to Hering the development of color theory proceeded along one main line, the latter originating a new branch which rivals, and, in the opinion of many, completely overshadows the parent stem. By a combination of characteristic features of both Young-Helmholtz and Hering theories, Donders directed development along a third line. At present therefore color theorists are divided into three groups, the physicists conservatively holding to the main line, the psychologists and physiologists, while divided in their allegiance, for the most part accepting the hypothesis of Hering.

The chief theories are criticised from the psychological standpoint in the "Dictionary of Philosophy and Psychology" art. 'Color Vision.' Several are also treated at considerable length in Sir Michael Foster's "Text Book of Physiology," and in Calkins' "Introduction to Psychology," as well as in other works of a similar character. To these and to the critical reviews by Mrs. Franklin which are referred to in their place, as well as to Dr. J. W. Baird of the Department of Psychology, Cornell University, I am indebted for valuable information.

PHYSICS DEPARTMENT. CORNELL UNIVERSITY.

## ON THE ASYMMETRY OF A MERCURY BREAK.

#### BY JAMES EDMUND IVES.

I N a paper, now in the course of publication, in the *Philosophical* Magazine, I have described a peculiar property of a mercury break. While making some experiments to determine the law governing the capacity of the shunted condenser necessary to stop the sparking at the break of an inductive circuit, I discovered that it depends upon the direction in which the current is flowing through the break. The arrangement of the experiment is shown

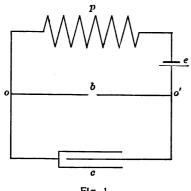
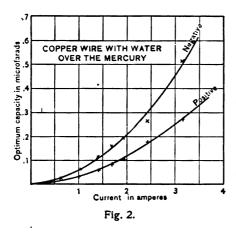


Fig. 1.

diagrammatically in Fig. 1, where p is a solenoid; e, a battery of one or more storage cells; b, a mercury break, and c, a shunted condenser. It will be noticed that the circuit consists of three branches: opeo', containing the solenoid and the battery; obo', containing the break, and oco', containing the condenser. The break, itself, was an amalgamated copper wire, a millimeter in

diameter, dipped by hand in and out of a small test-tube containing mercury. The test-tube was about two centimeters in diameter, and the mercury was covered with water to a depth of two or three centimeters. The least amount of capacity which must be inserted in shunt around the break to reduce the spark from a large to a small one, has been called, when the solenoid is the primary of an induction coil, the *optimum capacity*, and will be referred to by this name. further experiments to confirm it, and if possible to determine the cause of it. In the paper referred to, only one experiment dealing with this property of a mercury break is described, and the



constants of the branched circuit are not given. Eight new experiments have been made and the results of three of these, typical of all, are given in Table I.

The relation between the optimum capacity and the current, when the breaking pole is an amalgamated copper wire and the mercury is covered with water, is shown by the curves of Fig. 2, plotted

from the results of Experiment I, Table I. In these curves the asymmetrical behavior of the current is shown very clearly, the optimum capacity being much greater when the breaking pole is

Experiment 1. Amalgamated Copper Wire. Water over the Mercury.		Experiment 2. Amalgamated Copper Wire. No Water over the Mercury.			Experiment 3. Iron Wire. No Water over the Mercury.			
		n Capacity rofarads.	Current	Optimum Capacity in Microfarads.		Current	Optimum Capacity in Microfarads.	
in Amperes.	Pole	Breaking Pole Negative.	in Amperes.	Pole	Breaking Pole Negative.	in Amperes.	Breaking Pole Positive.	Breaking Pole Negative
.63	.018		.80	.038	.060	.70	.018	.038
.55		.020	1.00	.060	.092	.87	.024	.047
1.03	.033	.065	1.39	.105	.165	1.08	.035	.082
1.40	.060	.119	1.73	.155	.250	1.53	.070	.159
1.69	.084	.159	1.95	.195	.326	1.90	.117	.246
1.94	.104	.194	2.36	.261	.456	2.15	.134	.261
2.42	.177	.265	3.13	.412	.801	1	, '	
3.15	.274	.515		1	i	1	,	

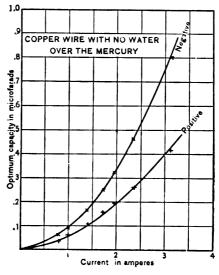
TABLE I.

negative than when it is positive. By the breaking pole "negative" is meant that it is connected to the negative side of the battery e. When "positive" it is connected to the positive side of the battery.

The change in the direction of the current through the break was made by commuting the connections to the battery. In all these experiments the electromotive force of the battery, consisting of

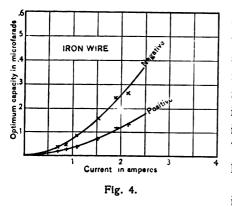
two storage cells, was 4.2 volts; the resistances of the branches *obo'* and *oco'* were each .1 of an ohm. The inductance of the solenoid, used in all the experiments without an iron core, was .000281 of a henry. The current was varied by inserting non-inductive resistance in the branch *opeo'*. The only inductive resistance in the branched circuit was that of the solenoid.

Thinking that this asymmetry might depend in some way upon the layer of water over the mercury, I made an



Flg. 3.

experiment without any water above it, and obtained the results shown in Experiment 2, Table I., and in Fig. 3.



It will be seen that the curves are essentially similar to those of Fig. 2. It then seemed that it might be due in some way to the amalgam in the copper wire, and an iron wire .87 of a millimeter in diameter was used instead. The results are given in Experiment 3 Table I. and in Fig. 4. The curves are similar to those of Fig. 2and Fig.

3. Since iron does not amalgamate under any circumstances, the effect is not due to the copper amalgam. In the same way a platinum wire was tried, and curves obtained similar to those of Fig. 4.

My first hypothesis was, that it was due to the fact that in the ordinary mercury break we have a spark passing between a point and a plane, the end of the wire being the point, and the surface of the mercury the plane. To test this, the break was made between an iron wire and a thread of mercury in a capillary tube. The diameter of the iron wire was .07 of a millimeter, and the diameter of the tube about a millimeter. The results obtained were similar to those of Fig. 4. Since, in this case, the break occurs between two points, and not between a point and a plane the effect is not due to this cause.

In seeking for an explanation it must be remembered that when the circuit *opeo'bo* is broken at b, an oscillatory current is set up in the circuit *opeo'co*. It seems possible that the asymmetry may be due to some selective action of the mercury vapor generated when the spark passes, of the same nature as the recently discovered Cooper-Hewitt effect. Or it may possibly be due to some capacity effect, such as is found in the Wehnelt interrupter.

I take pleasure in acknowledging the assistance rendered me in these experiments by Mr. Gordon Farnham, of the University of Cincinnati.

PHYSICAL LABORATORY, UNIVERSITY OF CINCINNATI, March, 1903.



## DO FALLING BODIES MOVE SOUTH?

BY EDWIN H. HALL.

PART I, HISTORICAL.

THE question whether a sphere falling from rest through a few hundred feet of still air swerves perceptibly toward the south, from the vertical path indicated by the plumb-line, is not, perhaps, one of the largest or most urgent problems of physics; but it has the dignity of venerable age and the charm of mystery. It was familiar to Newton; it has been answered in the negative, on theoretical grounds, by Gauss and by Laplace, and in the positive, on experimental grounds, by nearly every one of the investigators who have from time to time through more than two centuries made the actual trial.

If there is any significant feature of this problem, in its purely mechanical aspects, which Gauss and Laplace failed to perceive or could not adequately discuss, the discovery of this feature and its function is a worthy task for any mathematician of the present day. If there is any explanation in electric or magnetic action for a southerly deviation of perceptible magnitude, under the conditions of experiment which have prevailed, this explanation is yet to be offered by any physicist, though several have made the attempt. If the well-nigh universal agreement of experimental evidence as to the reality of such an effect is the result of a long succession of accidental errors in one direction, we have a striking exception to the ordinary course of chance events. If the whole mystery is the consequence of mental bias in the experimenters, the proof and explanation of this bias would have, at least, the merit of psychological interest.

Accordingly, it seems worth while to go over carefully all that is known in regard to the experiments in question, with a view to estimating, not merely the degree of skill and care shown in each, but also the mental attitude of each experimenter with regard to the issue of his work. In *Science* for November 29, 1901, Professor Cajori published an admirable summary of the history of our problem, describing briefly the results of all notable investigations upon it, whether experimental or theoretical. But for our purpose there is need of details which Professor Cajori did not give. Much of what immediately follows in regard to English investigators is taken from Mr. W. W. R. Ball's *Essay on Newton's Principia*.

In November, 1679, Robert Hooke wrote to Isaac Newton proposing a philosophical correspondence. The latter replied, declaring that he had "shook hands with philosophy," had "long grutched the time spent in that study," and was now busy with other affairs, but proposing a scrutiny of the course of falling bodies as a means of demonstrating the revolution of the earth. "Let Abe a heavy body suspended in the air, and moving round with the earth so as perpetually to hang over the same point thereof B. Then imagine this body . . . let fall, and its gravity will give it a new motion toward the center of the earth without diminishing the old one from west to east. Whence the motion of this body from west to east, by reason that before it fell it was more distant from the center of the earth than the parts of the earth at which it arrives in its fall, will be greater than the motion from west to east of the parts of the earth at which the body arrives in its fall; and therefore it will not descend the perpendicular . . ., but outrunning the parts of the earth will shoot forward to the east side of the perpendicular, describing in its fall a spiral line . . ., quite contrary to the opinion of the vulgar who think that, if the earth moved, heavy bodies in falling would be outrun by its parts and fall on the west side of the perpendicular." Newton added some very interesting suggestions as to the method of trying such an experiment. He would use a pistol bullet, on a calm day, would have the bob of the plumb-line "setled in water so as to cease from swinging," and would by preference work in "a high church or wide steeple, the windows being first well stopped; for in a narrow well the bullet possibly may be apt to receive a ply [push?] from the straightened [compressed?] air neare the sides of the well, if in its fall it come nearer to one side than to another."

On December 4 of the same year, Hooke laid Newton's pro-

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posal before the Royal Society, and an interesting discussion followed, in the course of which "Sir Christopher Wren supposed, that there might be something of this kind tried by shooting a bullet upward at a certain angle from the perpendicular round every way, thereby to see whether the bullets so shot would all fall in a perfect circle round the place where the barrell was placed."

On December II Hooke read to the society his answer to Newton's letter, maintaining that the course of the falling body "would not be a spiral<sup>1</sup> line, as Mr. Newton seemed to suppose," and "that the fall of the heavy body would not be directly east, as Mr. Newton supposed; but to the southeast, and more to the south than the east."

January 6, 1680, Hooke wrote to Newton : "In the meantime I must acquaint you that I have (with as much care as I could) made three tryalls of the experiment of the falling body, in every one of which the ball fell towards the southeast of the perpendicular, and that very considerably, the least being above a quarter of an inch, but because they were not all the same I know not which was true. What the reason of the variation was I know not, whether the unequal spherical figure of the iron ball, or the motion of the air, for they were made without doors, or the insensible vibration of the ball suspended by the thread before it was cut."

A little later Hooke answered Newton that "by two tryalls since made in two severall places within doors it [the same experiment] succeeded also," and on January 22, 1680, before the Royal Society, "Mr. Hooke showed the ball, that had been let fall from the hight of 27 feet, and fell into a box full of tobacco pipe-clay, sticking in the clay, upon the surface of which were made lines crossing each other : which showed the true perpendicular point indicated by the ball, when it hung suspended by a thread from the top, and how much the ball had varied from that perpendicular in its descent towards the South and East : and he explained the manner, how the same was performed in all particulars. It was desired, that this

might be witnesses of it before the next meeting. The time appointed was the Monday following at three in the afternoon." This apparently ends the account of Hooke's observations. He was Secretary of the Royal Society; and if his experiment had been successfully repeated before the witnesses proposed, it is altogether probable that he would have recorded the fact in some public form.

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In what has been quoted Hooke is entirely positive and somewhat circumstantial. Why is he not conclusive? Partly because his trials of the fall were so few, apparently only five in all, partly because the deviations which he recorded were so large in proportion to the very moderate height which he appears to have used. Moreover, Hooke, a brilliant genius but a somewhat uncertain character, had committed himself in the most open way to the opinion that experiment would reveal a southerly deviation. In a man of his reputation such a bias is not to be overlooked; and yet it is hard to believe that he deliberately lied to his associates of the Royal Society. His evidence is not to be altogether ignored.

Left in this dubious state by Hooke, our problem appears to have remained untouched for more than a century, until, in 1791, Guglielmini at Bologna took it in hand. He published a book in regard to the matter, but this book, if it exists still, is extremely rare, and few details of his work are now generally available. It was doubtless better than that of Hooke. He used a much greater fall, about 78 m., and appears to have made as many as sixteen trials. From these he deduced an average easterly deviation of about 1.9 cm. and an average southerly deviation of about 1.2 cm. He had a theory, whether formed before or after his experimenting the writer does not know, which attributed the southerly deviation to the resistance of the air. Indeed, his theory called for a somewhat smaller easterly deviation and a somewhat larger southerly deviation than his experiments produced.

But here, too, there were doubts. According to Benzenberg,<sup>1</sup> writing some twelve years later, "Guglielmini's experiments were

quotes Lalande as follows: "Guglielmini writes me that he is now convinced that Laplace is right, and that the theory gives no deviation toward the south. That which he has found toward the east agrees very well with the theory; but this is now no longer proof of the motion of the earth, since the other deflection, toward the south, does not at all agree."

In 1802 Benzenberg was much occupied with falling balls in the tower of St. Michael's at Hamburg. Most of his experiments were on the resistance offered by the air to such bodies, this resistance being deduced from the length of time occupied in a given fall as compared with the time which would have been required in a vacuum. He measured the duration of the fall by means of a watch at the top of the tower, and the paucity of experimental resources in those ante-electrical days is strikingly shown by the fact that he could not get this time for a height greater than a certain number of feet, perhaps 250, because, beyond this limit, he could not at the top of the tower hear the thud of the ball when it struck on a block of wood at the bottom. After these experiments on resistance he made, during the same year and in the same place, observations on the easterly and southerly deviations. For this purpose he dropped 32 balls, finding an average easterly movement of 0.90 cm. and a corresponding southerly movement of 0.34 cm. Was Benzenberg in undertaking this research prepossessed in favor of a southerly deviation? Possibly, for he knew of the work of Hooke and of Guglielmini, and he had not yet received from Gauss those letters which finally convinced him of the improbability of such a phenomenon. That he took the evidence of his own experiments seriously is shown by the fact that he did not at once yield to the authority of Gauss, but questioned whether some feature of the theory had not been overlooked. Later he appears to have received without opposition the suggestion, from Olbers, that air currents had affected the course of the balls dropped in the Hamburg tower. So far as the writer knows, this suggestion was entirely without proof.

way, developed the theory of a sphere falling from rest through still air under the influence of gravity alone, that is, without effect from magnetic, electric, or other obscure forces. Each pronounced the southerly deviation inappreciable, for experimental heights. It is not unlikely, therefore, that Benzenberg, when in 1804 he resumed his experiments on falling bodies, was affected by a strong prepossession against the existence of a perceptible southerly movement.

He worked now in the vertical shaft of a coal mine at Schlebusch, with a fall of 84.4 m. His preparations and arrangements were made with care and intelligence. To prevent air currents he covered the top of the shaft and stuffed the passage at the bottom with straw. He suspended each ball before its release by means of a horse hair gripped between the jaws of a vise, and, lest there should be a disturbing bulge in the hair just above the part flattened by the vise, he flattened the hair in advance by drawing it between two hot irons. "The sphere hangs by a flattened horse-hair in a closed space and beneath is an opening through which it falls at re-Together two crossed microscopes are brought to bear, in lease. whose common focus the horse-hair plays. . . . It takes always more than an hour, before a sphere comes quite to rest." "When the sphere is absolutely still, a light pressure opens the finely polished jaws of the vise, and the sphere falls." "Below lies a plank of wood [Packholz], which has in the middle a small hole through which the plumb-line of the point of suspension of the ball goes." Across the middle of the hole ran two threads, one of which marked the meridian, the other the parallel of latitude of the place. The ball made a sharply defined dent in the wood, and the distance of the middle point of this impression from both the meridian and the parallel was taken. Benzenberg remarks at one point that he has provided forty spheres for the research, and as these were probably made, like those he had previously used, of an alloy of the softer

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uniformly heated, air no such [southerly] deviation takes place, and the balls swerve only toward the east from the perpendicular." Cajori, who has apparently found some fuller account of this work than has come under the eye of the writer, says that "on selecting from the total number those experiments which, in his [Benzenberg's] judgment, were made under the most favorable conditions, there seemed to be no indication of a S. D."

The honesty of Benzenberg is not to be questioned. But we may well ask how far he may have been influenced, in "selecting" his evidence from the whole body of data, by the knowledge that the authority of Gauss and of Laplace was dead against the southerly deviation.

Whatever answer we may find for this question, the general belief among scientific men after 1804 must have been in accord with the opinion of the mathematicians, confirmed as it seemed to be by the work of Benzenberg. Accordingly, when Reich, in 1831, took up the problem which had been left undisturbed for nearly a generation, he can hardly, from previous evidence, have expected to find a deviation toward the south. He too worked carefully, profiting by the experience of his predecessors and making some changes of method which were possibly improvements. For example, he dropped his spheres, an alloy of tin, bismuth and lead, through a wooden spout erected especially for the purpose. The idea was good, as such a spout would prevent general horizontal draughts of air; but as we are told nothing about the size of the spout or the care taken to have the line of fall coincide with its axis, one may well be in doubt whether Newton's "ply from the straitened air neare the sides " was not in action here. Reich used sometimes the same method of release that Benzenberg had described and sometimes a curious method of his own "by means of an exactly horizontally placed ring, which was of such size that the balls when hot did not fall through it but when cold did fall through." He heated the ball in hot water, dried it, placed it on the ring and left it to fall through in its own good time. The defence of this unpromising device is that it seems to have worked better, causing less individual variation in the course of the balls,

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than the other. At the bottom of the fall Reich's arrangements were much like those of Benzenberg, already described. The height he used was 158.5 m., in the shaft of a mine at Freiburg. The following is a summary of his observations as at first recorded, though later the correction of an error in the direction of his meridian line reduced the mean southerly deviation about 0.07 cm.

Series.	No. of Balls.	<b>S.</b> D.	Probable Error
1	22	+0.6686 cm.	0.992 cm.
2	12	+2.3050 "	1.654 "
3	12	-0.1358 ''	1.572 ''
4	18	+1.2492 "	1.524 ''
5	21	-0.7881 "	0.606 **
6	21	-1.6017 "	1.413 "
	106	+0.5061 cm. [?]	0.27 cm.

Even with the correction for error of meridian Reich found a very considerable S. D., more than 0.4 cm. He had made a more extensive study of the problem, had dropped more balls, than any of his predecessors. Was the evidence he had found conclusive? No. If we were to omit his series 2, the one having the smallest number of balls and the largest probable error, we should have from the other five series not a southerly, but a northerly, deviation. The margin is too narrow.

Oersted, writing to Sir John Herschel a letter which was printed in the B. A. Report for 1846, makes interesting comments on the work of Guglielmini, Benzenberg, and Reich. He regards the work of the last as the best, but says that Reich's observations "differed much among themselves, though not so much as those of Dr. Benzenberg." He concludes : "After all this there can be no doubt that our knowledge of this subject is imperfect, and that new experiments are to be desired." He urges English men of science especially to this research, because of the superior facilities and resources for such work in England.

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devices used by his predecessors, and his own methods were crude, as the following account of them, given by himself in the *Mechanic's Magazine*, Vol. 48, 1848, will show :

"A strong rectangular frame was constructed, having a shelf or stage inside it, capable of turning freely upon an axis, supported by pointed centers, fixed in the sides of the frame. This frame was placed in a horizontal position over the shaft; and when the moment arrived for dropping the bullet, its support was suddenly removed by turning the stage round its axis.

"This plan, it is conceived, ensures the dropping of the bullet, without an appreciable tendency to any particular direction arising from the method employed. It may, perhaps, be objected that the cohesion between the shelf and the bullet would impart to the latter a motion in the direction in which the shelf moved. This is the case when the shelf is made to move very slowly, but when it is turned suddenly on its axis, even if it be some degrees from the truly horizontal position, no deviation arises from this source, as was clearly proved by preceding and subsequent experiments [not described].

"Besides the bullets, iron and steel plummets were used, the latter being magnetised. In form these were truncated cones, the lower and larger ends being rounded. These were suspended by short threads inside a cylinder, to prevent draughts of air affecting them, and when they appeared free from oscillation, the threads were let go. The number of bullets used was forty-eight and there were some of each of the following metals, iron, copper, lead, tin, zinc, antimony, and bismuth.

"A plumb-line was suspended at each end of the frame and east . and west of each other; to these were attached heavy plummets, the lower ends pointed. After they had been hanging for some hours in the shaft, a line joining their points was taken as a datum line from which to measure the deflection.

"The whole of the bullets and plummets dropped south of this datum line, and so much to the south that only four of the bullets fell upon the platform placed to receive them, the others, with the plummets, falling on the steps of the man-machine, on the south side of the shaft, in situations which precluded exact measurements of the distances being taken. The bullets which fell on the platform were from 10 to 20 ins., south of the plumb-line. E. H. HALL.

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"The deflection being much greater than I had anticipated could arise from any cause which appeared likely to produce a deviation, I feared the whole experiment was a failure, but more recent considerations have induced me to again test the method employed, [and] I feel confident that the deflection is not due to errors arising from the method of dropping the bullets, and that it is not at all likely that draughts of air in the shaft had any important influence on the result, but that there is a real deflection to the *south of the plumb line*, and that in a fall of a quarter of mile it is of no small amount."

A deviation of ten or twenty inches at the least, and nobody knows how much more, is large enough to be interesting. Unfortunately it is, as Rundell himself felt, hardly credible. Some grave fault of method or conditions is probable here. The manner of release of the bullets, by suddenly tipping the shelf on which they have been resting, is open to criticism, in spite of the confidence which he expresses in it. Indeed, this rather naïve confidence is the opposite of reassuring, as it seems likely that the sudden movement of the shelf would cause a disturbing current of air, if not some more direct mechanical action affecting the course of the bullets; and Rundell describes no experiments to justify his method in this particular. The fact, however, that the "plummets," which were released in a radically different way, all went far to the south, makes it probable, though not certain, that the main cause of the universal southerly movement in these experiments is not to be found in the method of release. The possibility of disturbing draughts of air is disposed of much too lightly by Rundell.

Moreover, we are told too little about the plumb lines, a criticism which applies to all the researches which have been reviewed in this paper. The lower end of a steel or iron wire would be deflected more or less, according to the weight of the plummet supported by it, from the vertical toward the north. Benzenberg probably used a silver wire; Reich used a copper wire. We are not told what kind of wire Rundell used, or Guglielmini, or Hooke.

Curious things may well occur when a plumb-line is suspended or a ball let drop in deep mine shafts not especially prepared for the experiment. Recent observations in the Tamarack, with a depth of more than 4,000 feet, showed two steel wires, carrying each a fiftypound weight, to be farther apart at the bottom than at the top.

Balls let fall in the same shaft, which is many feet wide, have, the writer is informed, apparently failed to reach the bottom, lodging somewhere on the way down. Air currents are now believed to explain the divergence of the plumb-lines, and air currents possibly may be responsible for the fate of the balls. The fact that a plumb-line in the shaft of an important mine may be at fault gives to our problem a suggestion of utilitarian interest.

In 1902 the writer made, in the inclosed tower of the Jefferson Physical Laboratory of Harvard University, by far the most elaborate and extensive research of which we have record on the course of falling spheres. Details of the method used will be given in another paper. The distance available was small, about 23 m., but the convenience of working in a well-equipped laboratory made possible a very large number of trials. After dropping some hundreds of balls in preliminary practice and development of details of procedure, the writer dropped 948 balls and took the mean deviations, to the east and to the south, for these cases. The result was, for the southerly deviation, 0.005 cm., about the five-hundredth part of an inch, with a "probable error" not much smaller.

If this result stood alone, it might well be considered as practically negative, discouraging belief in a southerly deviation. If the work of any other investigator in this field stood alone, it might well be disregarded, as raising no sufficient presumption in favor of the effect looked for to warrant the undertaking of further experiments. But the well-nigh invariable occurrence of an apparent movement toward the south,<sup>1</sup> the only exception being in the second research of Benzenberg, is a fact not properly accounted for by the history of our problem. Granting that Hooke was prejudiced and may even have merely pretended to find a southerly movement,

Observer.	Time.	Place.	Fall.	8. D.	<b>E.</b> D.	S. D. + E. D.
Hooke.	1680	London.	8.2 m.	+	+	?
Guglielmini.	1791	Bologna.	78.3	1.19 cm.	1.89 cm.	0.63
Benzenberg.	1802	Hamburg.	76.3	0.34	0.90	0.38
**	1804	Schlebusch.	84.4	0.	+	0.
Reich.	1831	Freiburg.	158.5	0.44	2.84	0.16
Rundell.	1848	Cornwall.	400.	25-50	?	?
Hall.	1902	Cambridge.	23.	0.005	0.149	0.03

<sup>1</sup>A summary of results is here given, S. D. standing for southerly deviation, and E. D. for easterly deviation :

granting that every experimenter probably wanted to find some deviation, a positive result in such a research being far more interesting than a negative one, granting that in a case like this, which presents great difficulties and uncertainties, a prejudice in favor of this or that result may lead the experimenter to look farther, so long as his expectation is not fulfilled, and to stop when his expectation is fulfilled—granting all this, the writer finds himself unable to remain quite content with the theory that these conditions have created out of nothing the general evidence in favor of a southerly deviation. Further investigation, under the best possible conditions, appears to the writer worth while, if only to establish a satisfactory negative, so that the question before us may vex no mortal more.

Where can these best possible conditions be found? Apparently in the great monument<sup>1</sup> at Washington. For something like a sheer five hundred feet this great pile has neither window nor crevice opening to the outer air. It can, therefore, be almost hermetically sealed against interior disturbance from winds. There is between the stairway and the elevator, on both the north and the south side, a clear space some thirty inches wide all the way from the "deck" at the top to the base.

But is not the top of so tall and slender a shaft all the time in a state of quiver which would give to the balls a lateral motion before their release, and thus cause them to wander widely in their long descent? Apparently not, at least when there is no wind. During a visit last January to the monument, the writer was surprised to find a mercury surface at the top much less disturbed than it commonly would be in the Physical Laboratory at Cambridge. The mud of the Potomac flats, in which the unfinished shaft once threatened to sink, has at least the merit of being an admirable insulator from the jar of traffic in the nearest streets, which, indeed, are a good distance No doubt, in a high wind the top of the monument would awav. quiver, and dropping balls in it in such a case, would be worse than labor wasted, for our present purpose. But, given a year, one might undertake there a research which should be conclusive, yielding a final answer to the question which stands at the head of this paper, a question which has been asked so many times in vain.

CAMBRIDGE, MASS.

<sup>1</sup> Cajori has suggested this place.

NEW BOOKS.

## NEW BOOKS.

Vorlesungen über theoretische Physik. Von H. von HELMHOLTZ. Band VI., Vorlesungen über Theorie der Wärme, herausgegeben von Franz Richarz. Pp. xii + 419. Barth, Leipzig, 1903.

The readers of the sixth volume of Helmholtz's "Theoretical Physics" are fortunate in having as editor of this, which is in some respects the most important portion of the great work of the master, one who had the opportunity of obtaining, at first hand, notes from Helmholtz's lectures as they were delivered to his classes in Berlin and who appreciated the importance of preserving so far as possible the form and personal idiosyncrasy of the original. Professor Richarz has performed this delicate and difficult task in a manner for which all those who have ever had the privilege of listening to the lectures of Helmholtz will be thankful. To such readers the volume will be found to have an especial charm. On nearly every page the personality of the author makes itself felt. This rare quality would inevitably have been lost had an attempt been made to supplement the original with new material. The highest value of such a book does not consist in striving for completeness or by bringing it up to date by the insertion of new matter, but in enabling us to see the subject as Helmholtz saw it and as he presented it in his lectures to his classes.

The task of presenting to the scientific public in a connected and consistent form the wealth of material which Helmholtz offered to his hearers throughout a long period was by no means a simple one. The presentation of the subject in the lecture room was not the same from year to year. His lectures also had a certain impromptu element, which while it did not detract from the interest or value of them, distinguished them, for example, from the perfectly systematized and fully developed courses given in theoretical physics in Berlin by Kirchhoff. Helmholtz was in the habit of taking up the subject, as it were anew, upon each occasion and of attacking his problem from whatever standpoint appealed to him at the moment. Professor Richarz is fortunate enough to have in addition to the stenographic report of the lectures as given in the winter of incorporating in the present volume a fuller and more comprehensive treatment of the subject than was given in any single year without introducing any element of discontinuity or lack of sequence. The volume includes as its chief subjects the conductivity of heat, the mechanical theory of heat, in the establishment of which the author had had in earlier years so important a part and the kinetic theory of gases, to the development of which he had likewise been one of the principal contributors. E. L. N.

A Treatise on the Theory of Solution Including the Phenomena of Electrolysis. By W. C. D. WHETHAM. Pp. 475. The University Press, Cambridge, 1902.

This volume is an outgrowth of the smaller book "Solution and Electrolysis," published in 1895. There is a preliminary chapter on thermodynamic principles; then follow chapters on the application of the phase rule to one-component and two-component systems. General solubility relations are next considered and then comes a discussion of osmotic pressure. The author is then in a position to discuss quantitative relations between concentration and change of vapor pressure. The results are summoned up in a chapter on theories of solution. This is an orderly and logical development of the subject.

Having established the general facts in regard to solutions, the author considers electrolysis, conductivity of electrolytes, galvanic (better voltaic) cells, contact electricity and polarization. After this comes the theory of electrolytic dissociation, diffusion in solutions and solutions of colloids.

This is a very interesting book and shows a general sanity of treatment which we do not always find in books of this sort. On p. 128 the juggling with the molecular weight of the liquid is unfortunate and misleading. The table of electro-chemical properties of aqueous solutions printed as an appendix is admittedly ten years old.

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## Niels Henrik Abel, Memorial Publie a L'Occasion du Centenaire de sa Naissance, Kristiania. By JACOB DYBWAD. 1902. (Received.)

Die Theorie der Collectivgegenstande. By GOTTL. FRIEDR. LIPPS. Pp. i + 215. Leipzig. Verlag von Wilhelm Engelmann, 1902. (Received.)



## ТНЕ

## PHYSICAL REVIEW

# A DETERMINATION OF THE HEAT OF FUSION OF ICE.

#### BY ARTHUR W. SMITH.

#### INTRODUCTION.

A<sup>T</sup> the present time there is no constant of nature of greater importance, and at the same time less well known, than the heat of fusion of ice. One naturally refers to the classic researches of Regnault, and to the later determination of Bunsen as fully determining this constant. But a comparison of the values obtained by these two investigators shows that they differ by I part in 100, and a more critical examination of the original memoirs is sufficient to convince one that neither determination is all that could be desired. Determinations made by other investigators, while agreeing well among themselves, give results which differ considerably from each other. At the present time it is safe to say that the heat of fusion of ice is known only to I part in 200. This wide variation was pointed out three years ago by Professor J. S. Ames<sup>1</sup> in his paper on the "Mechanical Equivalent of Heat," and at that time he suggested to the writer the need of a more exact determination of this constant. It was not until the present year, however, that it was possible to take up this investigation and carry it through.

The whole subject of calorimetry must be regarded as still in its infancy as long as its measurements are expressed in variable and unknown units. The usual unit employed, viz., the gram-degree <sup>1</sup>Paris Reports, 1900, Vol. I., p. 178.

calorie, can never become a satisfactory standard for the measurement of quantities of heat inasmuch as it involves the measurement of changes in temperature of some substance and all the inherent uncertainties connected with such measurements. This is doubly true when the substance employed has a varying heat capacity, as is the case with water. A far more satisfactory unit would be one expressed in terms of the heat required to produce a change of state without any attendant change of temperature. The most convenient unit for practical purposes and fulfilling these conditions, is found in the heat of fusion of ice, and it is surprising that no determination of this very important constant has been attempted for a third of a century, and that no electrical method has ever been used.

Electrical measurements have now attained such a degree of perfection that the heat generated by an electric current can be determined with an accuracy far surpassing any direct calorimetric method. The problem which I have undertaken to solve is the determination of the heat of fusion of ice in terms of the electrical units.

## PREVIOUS DETERMINATIONS.

The fact that when heat is given to a piece of ice its temperature is raised until  $0^{\circ}$  C. is reached, at which point it remains while large quantities of heat continue to be added, was first pointed out by Black<sup>1</sup> in his remarkably clear and explicit lectures on chemistry delivered in Edinburgh in 1762. The heat which was thus used in melting the ice without producing any change in temperature was called by him "latent heat," a name which, although not altogether felicitous, has clung to it ever since.

Black determined the amount of this "latent heat" by several methods. In one experiment he measured the time required for the conversion of a known quantity of ice at  $32^{\circ}$  F. into water at  $40^{\circ}$  F. in a room of which the temperature remained constantly at  $47^{\circ}$  F., and compared it with the time during which the temperature of

 $32^{\circ}$  F. were melted in 135 parts of water at 190° F., giving 254 parts of water at 53° F. Hence taking into account the different specific heats of the water and the containing vessel, he deduced the number 143° F. In a third experiment, which is really a modification of the latter, the water was warmed to 176° F. and mixed with an equal weight of ice. The resulting mixture was water at  $32^{\circ}$  F., giving for the heat of fusion the number 144° F. The last two methods are much more accurate than the first, and give the mean value 143°.5 F. or 79°.7 C.

A few years later Wilke, a Swede, determined the heat of fusion of ice by a different method. He took two similar vessels, one filled with water at  $0^{\circ}$  C. and the other with an equal weight of snow at the same temperature, and placed them both in boiling water. When the thermometer in the first vessel reached 72° C. he quickly removed the second, assuming that it had received the same amount of heat as the first. The temperature indicated was  $+ 2^{\circ}$  C. and a bit of the snow was unmelted. This soon melted, reducing the temperature to  $0^{\circ}$  C., and therefore Wilke took the number 72 as representing the heat of fusion of the snow. The inherent errors of this method are so great the wonder is that they balance each other as nearly as they appear to do.

The first determination of the heat of fusion of ice worthy the name was made in 1780 by Laplace and Lavoisier.<sup>1</sup> In their work on specific heats they used an ice calorimeter consisting of an inner chamber surrounded on all sides by finely broken ice. This ice was protected from outside heat by another covering of ice. A warm body placed within the chamber would melt some of the surrounding ice, the resulting water being allowed to drain away to where it was collected and measured. Equal weights of different substances, when warmed to the same temperature and placed within the calorimeter, were found to melt different amounts of ice in cooling to  $0^{\circ}$  C. By comparing the amounts of ice thus melted the relative specific heats of different substances were obtained.

In order to express these results in terms of water it was necessary to determine the amount of ice which would be melted by a

<sup>1</sup> Lavoisier et Laplace, Memoires de l'Academie des sciences, 1780, p. 355; Oeuvres de Lavoisier, t. I., p. 283.

given amount of water in cooling one degree. A vessel of sheet iron, weighing with its cover 1.7347 pounds, was filled with water, 2.74349 pounds, and placed in boiling water. The temperature attained was  $79^{\circ}.5$  R. The vessel with the hot water was transferred to the interior of the ice calorimeter, and at the end of sixteen hours it had reached the temperature of the ice. The amount of ice melted was 3.966797 pounds, of which 0.232219 pound was due to the sheet-iron vessel, determined by a separate experiment. The ice melted by the hot water was, then, 3.714578 pounds. (Doubtless these figures were obtained by calculation, and do not imply extreme accuracy.)

In another experiment the warm water was poured into the calorimeter and, apparently, directly upon the ice. The amount of water used was 4 lb. 8 oz. at  $70^{\circ}$  R. There was removed from the calorimeter 9 lb. 12 oz. of water at  $0^{\circ}$  R. Hence 5 lb. 4 oz. of ice was melted by the 4 lb. 8 oz. of water. In order to have melted an equal weight of ice the temperature of the water should have been  $60^{\circ}$  R. Another experiment gave the number  $60^{\circ}.856$ . The mean of these values, "and several others" not published, was taken in round numbers to be  $60^{\circ}$  R. This is equivalent to  $75^{\circ}$  C., and this value of the heat of fusion of ice was accepted and used by physicists for the following sixty years — from 1780 till 1840 or later.

The first determination of the heat of fusion of ice which bears the marks of accuracy is that of La Provostaye and Desains,<sup>1</sup> in 1843. These investigators used the method of mixtures, strictly so called. That is, pieces of ice from the surface of which most of the water had been removed with tissue paper, were dropped into water and the lowering of temperature caused by the melting of the ice was measured with a thermometer. Their thermometers were graduated to tenths of a degree and read to hundredths, and were compared with standards. The amounts of water and of ice

amount of ice used in the experiment the final temperature would be nearly the same as that of the surroundings. By this means the radiation correction of the calorimeter was made as small as possible. The rate of cooling of the calorimeter for each degree difference in temperature between the water in the calorimeter and the surroundings was determined by a preliminary experiment. During an experiment the temperature was recorded every few seconds, and the observed final temperature was corrected for the cooling by radiation.

They estimated the amount of water clinging to the ice as about one two-thousandth of the weight of the ice, and as therefore too small to take into account in their experiments. The mean of seventeen determinations of the heat of fusion of ice gave the value 79.01 calories in terms of the mean specific heat of water over the range 10° C. to 24° C. The authors show that this value is subject to a probable error of 0.30 calorie.

The weights of the calorimeter with the water and the ice were corrected for the loss due to evaporation. The loss of heat due to this cause if taken into account at all may have been included, consciously or unconsciously, in the determination of the rate of cooling. But in the single detailed calculation given, if an amount of water as great as assumed, and by which the weights are corrected, actually did evaporate, the cooling produced thereby would be 160 per cent. of the total cooling correction applied.

The results obtained by La Provostaye and Desains were confirmed by the experiments of Regnault<sup>1</sup> made the same year. He also used the method of mixtures and pointed out the errors due to the water introduced on the ice, and to the evaporation of water from the calorimeter. No corrections were made, as these were considered too small to affect the result. This is true regarding the change in weight, as the maximum evaporation was only 0.07 gram, but the heat required to evaporate this water, if neglected, would make the computed value of the heat of fusion too great by one third of a unit.

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degree below  $0^{\circ}$  C. When transferred to the calorimeter the snow melted very quickly, thus reducing the errors due to radiation. The specific heat of the snow was assumed to be the same as for water. The mean of four determinations gave the result 79.24 calories.

There being little snow in Paris the following winter, he used pieces of ice cut from a clear block and free from air bubbles. The ice was dried with filter paper and quickly transferred to the calorimeter, its mass being determined by weighing the calorimeter before and after the experiment. The mean of thirteen determinations was 79.06 calories, in terms of water over a mean range of from  $11^{\circ}$  C. to  $22^{\circ}$  C.

In 1848 Hess<sup>1</sup> conducted an elaborate series of experiments to determine the heat of fusion of ice. He avoided the errors introduced by the layer of water on melting ice by using ice several degrees below zero. The room in which he worked was kept cool, while the balance, ice, etc., were in a glass case outside one of the northern windows. The temperature of the ice was measured by a thermometer in the midst of broken pieces in a beaker. The usual method of mixtures was used, the cold ice being placed in the water and allowed to melt. The temperatures were measured to tenths of a degree, and the amounts of ice and water so proportioned that the final temperature was that of the room. Forty determinations were made, each involving the two unknown quantities, the specific heat of ice and its heat of fusion. Solving for these quantities gave 0.533 for the specific heat of ice, and for the heat of fusion the value 80.34 calories in terms of water over the mean range of from 7° C. to 19° C.

The last investigation having as its object the determination of the heat of fusion of ice was made in 1850 by Person.<sup>2</sup> He criticises the values found by Regnault and La Provostaye and Desains because they had followed the methods of previous investigators

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Person used the method of mixtures, the temperature of the water being about  $+ 16^{\circ}$  C. and that of the ice from  $- 2^{\circ}$  C. to  $- 21^{\circ}$  C. The ice was a cylindrical block, 4 cm. in diameter and 12 cm. high. This was enclosed in a sheet-iron case and contained a thermometer to measure its temperature. The specific heat of the ice was determined by cooling it to  $- 21^{\circ}$  C. in a freezing mixture, then plunging it, case and all, into the calorimeter, which contained a saline solution a few tenths of a degree below  $0^{\circ}$  C. After ten or twenty minutes the final temperatures were read. Two determinations gave 0.48 for the mean specific heat of ice from  $- 21^{\circ}$  C.

The experiments for the determination of the heat of fusion of ice were conducted in a similar manner. The block of ice was cooled in a freezing mixture to several degrees below  $0^{\circ}$  C. and then plunged into the calorimeter, which contained water at about  $16^{\circ}$ C. Using the above value for the specific heat of ice, and unity for the specific heat of water, he obtained the value 80.0 for what he was pleased to call the "total" heat of fusion, this being the mean of six experiments. From the recorded data it is impossible to say what the error of this result may be. The only corrections applied are for the water equivalent of the calorimeter, thermometer, etc., and a correction for radiation—the determination of which is not given.

In 1870, Bunsen<sup>1</sup> devised the ice calorimeter which bears his name. As with the ice calorimeter of Laplace and Lavoisier, Bunsen used his instrument for the study of specific heats, and in order to express the specific heats of the substances studied in terms of the mean specific heat of water two auxiliary experiments were made. In these experiments he used 0.3333 gram of water enclosed in a glass tube and warmed to the temperature of boiling water. The water and tube were then dropped into the ice calorimeter, and the change in the scale reading observed. In the second experiment the same water and tube were warmed to identically the same results, 80.01 and 80.04, of necessity agree very closely. The mean, 80.02, is expressed in mean calories.

The results of these determinations are collected in Table I. It

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Name.	Date.	Number of Experi-	Temp.	Heat of Fusion.	
		ments.	Range of Water.	Calories.	Joules
Black.	1762	2	80-0	79.7	
Wilke.	+	1	720	72	
Laplace and Lavoisier.	1780	2	100-0	75	
Provostaye and Desains.	1843	17	24-10	79.1	331.5
Regnault.	1842	4	16-7	79.24	332.7
Regnault.	1843	13	22-11	79.0 <del>6</del>	330.8
Hess.	1848	40	19-7	80.34	337.1
Person.	1850	6	16-5	80.0	335.9
Bunsen.	1870	2	100-0	80.02	335.2

Summary	of	Previous	Determinations.
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is difficult to determine the exact temperature of the water used in these experiments but the attempt has been made to express the results in terms of joules, by making use of Barnes' values of the mechanical equivalent of heat, and the values set down in the table can not be far from right.

In all of these determinations of the heat of fusion of ice practically a single method has prevailed, that of mixtures. The limitations of this method are at once evident. No knowledge of the condition of the ice when it enters the calorimeter is possible. Unless it is melting, and has been in that condition a very long time, its temperature is entirely unknown. Experiments show that a block of ice which has been for several hours in a warm room (20° C.) may still be considerably below 0° C. in the interior. If such a block is broken up and soon used, even the small pieces will be colder than 0° C., although melting on the exterior. Again when the ice has been melting long enough to insure its temperature being very close to 0° C. it is impossible to remove all of the water from the ice, and an unknown amount of water is thus carried into the calorimeter and credited up as ice. It is not necessary that this water should be solely that of the superficial layer covering the Unless the ice has been formed from exceedingly pure water. ice.

and is uniform throughout, melting will occur at interior places, the resulting water remaining in its own cavity. The amount of water which may thus exist throughout the ice is neither determined nor removed, but is counted as so much ice.

Moreover, this method involves the measurement of changes in temperature, which at best involves considerable uncertainty, especially when mercury thermometers are used; and as the results are expressed in indefinite units, the whole subject has been left in a most unsatisfactory condition.

## GENERAL METHOD.

The method employed in the experiments now to be described may be briefly stated as follows: The sample of ice, whose heat of fusion is to be determined, is broken into small pieces and cooled several degrees below o° C. While at this temperature it is weighed and transferred to the calorimeter, which contains kerosene oil also two or three degrees below o° C. In this state there can be no question that the ice is entirely free from water, either on the outside or interior. The calorimeter and contents are slowly warmed by a very small electric current until the temperature reaches the desired point for commencing an experiment, usually about  $-1^{\circ}$  C. A larger current is then applied for sufficient time to melt the ice and raise the resulting water to about  $+ 0^{\circ}.5$  C. At this temperature (of equilibrium) the ice has certainly all been melted, and the heat generated by the current has been used in four ways: (1) In raising the temperature of the ice and the calorimeter from about  $-1^{\circ}$  C. to  $0^{\circ}$  C.; (2) in melting the ice; (3) in raising the temperature of the water and calorimeter from 0° C. to about  $+ 0^{\circ}.5$  C., and (4) in supplying whatever heat is lost by the combined effects of radiation, conduction, convection, etc. Of these four quantities of heat the second is thirty or forty times as great as all the others combined, which are determined as corrections, and when subtracted from the total amount of heat generated by the current, gives the heat required to melt the ice. This amount of heat divided by the mass of the ice gives the heat of fusion per gram of ice.

In order to provide a medium for the transference of heat from

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the wire carrying the current to the ice, and to enable the different parts of the calorimeter to attain an equilibrium temperature, a bath of refined kerosene known as "Pratt's astral oil" was used. This oil could be cooled to any desired temperature without losing its fluidity, and it had no action on the ice — two points which are only possessed by this fluid, as far as could be learned.

The amount of heat produced in the heating coil by the current was determined by measuring the difference of potential between the terminals of the coil, the current which flowed through it, and the time during which the current was flowing. The heat, in joules, is then given by the formula *Elt*.

Each experiment is naturally divided into three parts: (1) The determination of the heat capacity of the calorimeter, ice, oil, etc.; (2) the melting of the ice, and (3) the determination of the heat capacity of the calorimeter, water, oil, etc. These are discussed in . order below.

Heat Capacity of the Calorimeter, Ice, etc.— The amount of heat required to raise the ice, oil, calorimeter, etc., from the initial temperature to  $0^{\circ}$  C., was determined from the rate of warming during the preliminary heating. The current used for this was one tenth as large as that employed in melting the ice, thus generating one hundredth as much heat per minute. This small amount was used in order to warm the ice slowly and without melting any of it. As  $0^{\circ}$  C. is approached it was more and more difficult to apply heat and not allow any portion of the oil, even close to the wire, to become warmer than  $0^{\circ}$  C., but with care there was never any trouble from this source when the temperature was as low as  $-1^{\circ}$  C.

The heat capacity of the entire apparatus, including the ice, was found as follows: The temperature was read every minute, while the ice and oil were constantly stirred, until the rate of warming due to the combined effects of radiation, conduction, convection, stirring, etc., was nearly constant for ten or fifteen minutes. Then the small current was passed for ten minutes, the stirring being continued at the same rate, while the temperature rose more rapidly.

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while the current was flowing, by Newton's law, which is shown below to apply to this case, is the mean of the rates just before and just after (since the temperature, on the average, is a mean between the temperatures before and after). The total amount of heat received by the calorimeter and its contents causes a certain rise of the thermometer, and since the temperature at the beginning and the end is changing very slowly it is safe to assume that the thermometer indicates the temperature of each part of the calorimeter, including the small pieces of ice. The difference between this observed change in temperature and that which would have been produced during the same time by outside influences alone, gives the change in temperature due to the current. This establishes the relation between heat (expressed in joules) and the change in temperature produced by the addition of this amount of heat. On the assumption that the same amount of heat will produce the same temperature change at any temperature up to 0° C., it is a simple matter of proportion to find the number of joules required to raise the calorimeter and contents from the initial temperature to 0° C. That this assumption is fully warranted is shown by experiments given below.

Melting the Ice. — The first part of the experiment is followed directly by the second, which differs from it only in the quantity of heat employed and the consequently greater changes in temperature, together with the melting of the ice. The current is about two amperes and flows for twenty or thirty minutes, while the stirring continues uninterrupted at the same rate as before. Two observers are required during this portion of the experiment — one to continue the stirring and read the thermometer and keep the records, while the other attends to the regulation and measurement of the electrical energy.

In series with the heating coil was placed a standard half ohm coil which was specially designed for carrying currents as great as two amperes. The current through these coils was maintained

was measured with a potentiometer and standard cell. The time during which the current was flowing was measured with an Elgin watch with the aid of a reading glass. This measurement of both the current and the difference of potential makes the experiment more complicated and laborious than it would have been simply to maintain a constant current through the coil and calculate the heat from the formula  $RI^2t$ , where R denotes the resistance of the heating coil, or to maintain a constant E.M.F. and calculate the heat from the expression  $E^{2}t_{l}R$ . In each of these cases a knowledge of the resistance R would be required, and this is unknown without a knowledge of the temperature of the wire when carrying the current. This temperature may be several degrees warmer than the surrounding bath and in any case is very difficult to determine. All of this uncertainty regarding the resistance of the heating coil is avoided by the method here adopted, and the increased labor is more than repaid in the increased confidence in the measurement of the electrical energy.

Heat Capacity of the Calorimeter, Water, etc. — After the ice is melted and the current stopped, the water, oil and calorimeter come to some equilibrium temperature a few tenths of a degree above  $o^{\circ}$  C. The amount of heat which has been expended in raising the temperature above  $o^{\circ}$  C. is found by another experiment in all respects similar to that performed below  $o^{\circ}$  C., and just described. The heat capacity will, of course, be greater than before, since the calorimeter now contains water instead of ice. It has been shown by Barnes<sup>1</sup> that the specific heat of water exhibits no peculiarity in the neighborhood of  $o^{\circ}$  C., and therefore within the limits of accuracy here required, the heat capacity of the entire apparatus is the same at about  $+ o^{\circ}.6$  C. that it is over the range from  $o^{\circ}$  C. to  $+ o^{\circ}.5$  C.

Correction for Radiation, Conduction, Convection and Stirring. — There remains another important correction, viz., the heat lost to the calorimeter by radiation, conduction, convection, stirring, etc., during the period in which the ice is being melted. This is determined in much the same way as in the auxiliary experiments just described. The bulb of the thermometer is near the wall of the calorimeter and

<sup>1</sup> Barnes, PHYSICAL REVIEW, Aug., 1902.

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it is assumed that the temperature of one represents the temperature of the other. Newton's law of cooling is assumed, that is, that the heat lost each minute is proportional to the difference in temperature between the wall of the calorimeter and the surroundings. From the data already obtained the rate of cooling (or warming) at several temperatures both above and below o° C. is given. These rates of cooling are expressed in terms of the equivalent joules per minute and plotted as ordinates against the corresponding temperatures as abscissæ. The curve joining all these points is very nearly a straight line, and if Newton's law is true it should be absolutely a straight line. Therefore the straight line which lies nearest to the plotted points is drawn, and this line then gives the heat lost per minute at any temperature.

The heat lost by the calorimeter through the combined effects of radiation, conduction, convection, stirring, etc., during the interval in which the ice is melting is then obtained from this curve as follows. As the temperature is measured each minute, the average of these readings gives the mean temperature during the experiment. The ordinate on the curve corresponding to this temperature gives the mean loss of heat per minute This quantity multiplied by the time in minutes gives the total loss of heat by radiation, etc.

#### DESCRIPTION OF APPARATUS.

In devising a form of apparatus suitable for the accurate determination of the heat of fusion of ice, two things were especially desired. First, that it would admit using different samples of ice, and ice formed under different circumstances, and secondly, that it should have as small a radiation constant as possible. The first condition debarred the Bunsen calorimeter, or any similar instrument, even if it had not been shown<sup>1</sup> that the density of ice depended upon the method of manufacture, and therefore rendered this instrument incapable of accurate results.

After a number of preliminary experiments upon the radiation constants of different calorimeters (*i. e.*, the heat lost or gained per minute per degree difference of temperature between the calorimeter and its surroundings) it was found that the best protection

<sup>1</sup> Nichols, PHYS. REV., Vol. 8, pp. 21-37, 1899.

against radiation was the double wall of a Dewar bulb. Accordingly a half-liter Dewar bulb was used for the basis of the calorimeter. This was supported within the chamber D, Fig. 2, by a special wooden clamp which fitted around the neck of the bulb. The upper portion of this clamp passed upwards through the tube T, which it completely filled and by which it was supported. The thermometer, stirrer rod, and current leads passed through appropriate holes, drilled lengthwise in this clamp support.

This form of calorimeter proved very satisfactory and fulfilled the highest expectations regarding the loss or gain of heat by conduction and radiation. When filled with water a few degrees below the surroundings it warmed up at the rate of  $0^{\circ}.0016$  C. per minute per  $1^{\circ}$  C. difference in temperature between the interior and the exterior.

A preliminary experiment to see how rapidly ice could be melted without unduly raising the temperature, was performed as follows: Since only qualitative results were desired the bulb was filled with water instead of kerosene, and about a hundred grams of broken ice dropped in. On supplying heat by a current through the coil, the gratifying result was obtained that 50 watts raised the temperature to only  $+ 0^{\circ}.5$  C. In other words, ten grams of ice could be melted per minute without raising the temperature over  $0^{\circ}.5$  C. and consequently without producing much loss of heat by radiation.

But this fair beginning was doomed to speedy disappointment. In the midst of the next experiment, the inner wall of the bulb exploded with a loud report, the contents and broken glass being caught and held by the outer wall, which did not break. No possible reason could be found why the bulb should have given away at just that time. Fortunately the thermometer, which was within the bulb, escaped uninjured. Several weeks were spent in trying to obtain a duplicate bulb. The first one obtained had a much smaller neck, and while superior to the original in some respects it could not be used on the same supports, and did not give sufficient space for the thermometer, stirrer, current and potential leads, etc. After much correspondence, a bulb was obtained very like the original, and the experiments were resumed.

On trying the complete experiment and using kerosene as the

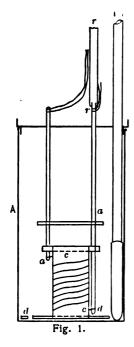
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fluid, the ice, as expected, sank to the bottom of the bulb. When the current was passed to melt the ice, the temperature was found to be much higher than it was in the preliminary experiments in which the ice floated at the top of the warm fluid (water). This was doubtless due to the warmer oil rising to the top and away from the ice, which remained in a more or less compact mass at the bottom and presenting a minimum of surface to the action of the oil.

Many ineffectual attempts were made to support the ice in the oil with the heating coil below it. Various kinds of stirrers were tried in hopes of securing a more thorough circulation of the oil amongst the pieces of ice, but with limited success. The principal difficulty was in the smallness of any arrangement which could be passed through the neck of the flask. Finally, almost by accident, a form of rotary stirrer was found which secured complete circulation and promised satisfactory results. But disappointment was again in store. One day as the bulb containing some oil was resting upon the bed of excelsior where it was kept when not in use, a loud report was heard, and that bulb was no more. The destruction was complete, some of the pieces being thrown a distance of a meter away. I was only thankful it did not occur when in use, with the delicate thermometer inside.

Of course another bulb could have been obtained, but the danger of its exploding at any moment, and especially the risk of destroying the thermometer, was so great, it was decided to use some more stable form of apparatus. Moreover it was now the first of January with cold weather approaching, during which all the experiments would have to be performed. The shortness of time forbade much waiting for the construction of elaborate apparatus, and, therefore, the best that lay at hand was tried. While not equal to the Dewar bulb in preventing loss of heat by radiation, still it was very good, and the certainty of its remaining intact fully balanced any inferiority in other respects.

Final Form of Calorimeter. — The calorimeter as finally used is shown in section in Fig. 1, which is nearly self explanatory. A is ered, manganin wire. The wire is insulated from the tube by a double thickness of silk, and the whole covered with several coats of shellac well baked on. The ends of the coil are soldered to two heavy copper leads, *aa*, to the upper ends of which are soldered the current and potential leads. The stirring is effected by a disk of brass, *dd*, which nearly fits the calorimeter, and is soldered to the lower (nd of the brass tube, *cc*. It is perforated by a number of small holes through which some of the oil can circulate while the greater part of it streams through the heating tube as the stirrer is moved up and down. The stirrer rod, *rr*, is a hard-rubber tube



which screws onto the end of one of the heavy copper leads. It extended upward to the outside alongside the thermometer, Th, and also served to support the current and potential wires.

On one or two occasions during the preliminary experiments a few drops of oil were found to have spilled out of the calorimeter, which of course would seriously affect the weight of the apparatus at the end of an experiment, to say nothing of the change in the heat capacity. To prevent this as far as possible a tightly fitting cover was made. Openings were necessary for the thermometer, the stirrer rods, and for the tube through which the ice was dropped. A lid was arranged to fall and cover the latter opening when the tube was withdrawn. An edge was placed around the cover to hold whatever oil might find its way to the top. This precaution

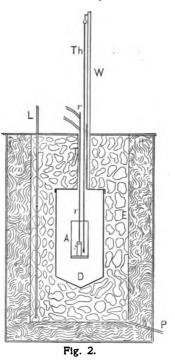
may have been unnecessary, as no oil was ever found on the cover.

The calorimeter was supported in the following manner. Sufficient cotton wool was wrapped around it to just slip into a large glass battery jar. This jar rested upon a wooden block at the bottom of the chamber D, Fig. 2, and to prevent as far as possible the loss of heat by convection air currents the remaining space was filled with cotton wool.

The dimensions of this chamber are 35 cm. in depth by 23 cm. diameter, it being circular in section. The larger vessel, E, is 70 cms. deep and 45 cm. in diameter, it also being circular in section. Both of these vessels were made of heavy galvanized iron. The space between them was filled with broken ice, making a layer 11 cm. in thickness around the sides of the inner chamber, and about

twice this thickness over the top and bottom, thus maintaining the temperature of the interior chamber very closely to 0° C. The top of this chamber is a removable cover, made with an outside flange to prevent water from gaining access to the inside. At the center of this cover is a tube 4 cm. in diameter and 20 cm. in length, which extended through the broken ice to the outside, and through which passed the thermometer, stirrer rod, current wires, etc. In order to protect this broken ice as much as posr sible from outside heat, the vessel Ewas placed within an extra large barrel with the intervening space packed with excelsior. With this protection the amount of ice melted was about ten kilos per day, this amount being

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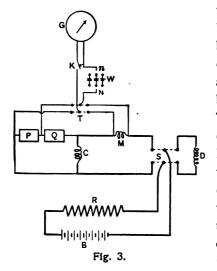


added each morning. The total quantity of ice required for this packing around the chamber was about sixty kilos. As fast as it melted the water was drained away through the tube P. Over the barrel was a wooden cover through which projected the tube T, the wooden post, W, which served as a support for the thermometer when in use, and the thermometer case, L, in which the thermometer ter was kept during the time between experiments.

In order to fill the calorimeter with oil and ice a thin brass tube was arranged parallel to the thermometer and extending from the outside to about half a centimeter below the cover of the calorimeter. Within this tube was a glass funnel through which the cold A. W. SMITH.

oil was poured. The funnel was then removed and the ice dropped through the tube, after which the tube was removed, the small trap door falling and closing the opening in the cover. The tube T was then filled with cotton to prevent circulation of the air between the inner chamber and the outside, it being firmly packed around the thermometer and stirrer rod, but allowing the necessary motion of the latter.

Electrical Arrangements. — A diagram of the electrical connections is shown in Fig. 3. C is the heating coil within the calorimeter, M is the standard half-ohm coil, while D is an auxiliary coil of resistance equal to C and M together. The current was obtained



from eight storage cells, B, and by means of the switch S, could be passed through the auxiliary coil D while it was adjusted to approximately the proper value by the variable resistance R. The latter consisted of a rheostat containing a total of six ohms of heavy iron wire, in parallel with which was a liquid resistance of copper sulphate solution. By this means as small variations in the current as desired could easily be made. When ready to use the current in the calorime-

ter, the double pole, double throw switch S was closed on the other side, and the current quickly brought to the proper value by a very slight adjustment of the resistance R.

The galvanometer, G, was the Rowland D'Arsonval wall type and quite sensitive. Its free period of vibration was about 15 seconds, with little damping and requiring several minutes to come to rest

between the poles of the permanent magnet; and the coil of the galvanometer was short-circuited by the key K when open. These three methods of damping rendered the galvanometer sufficiently dead beat to be used, if care was taken never to allow deflections of more than 20 mm. Usually, however, the deflections were about 1 or 2 mm.

Three Weston standard cells, W, were used for the measurement of the current and E.M.F. They were connected to three pairs of mercury cups, as shown, and any one of them could be inserted in one of the galvanometer leads by placing the wires, nn, into the corresponding mercury cups. The ends of these wires were fastened in a block of hard rubber and projected about a centimeter beneath. By simply lifting this block from one pair of cups to another any one of the standard cells could be brought into use. One cell was used throughout one experiment (about half an hour), during which interval its constancy was several times tested by substituting an unused cell in its place for a single reading. No sign was ever found that the cells suffered the least change in their E.M.F. when in use. These cells were certified to have a constant E.M.F. at all temperatures between 10° C. and 35° C., but they were always used at very nearly 20° C.

The absolute value of the E.M.F. of these cells was determined by the National Bureau of Standards, where one of these cells (No. 329) was compared with ten standard Clark cells. Assuming the Clark to be 1.434 volts at  $15^{\circ}$  C. the E.M.F. of this cell was found to be 1.0193 volts at  $18^{\circ}$  C.

The results of all the experiments, save two, are expressed in terms of this cell. In the other two the standard cell No. 328 was used, the E.M.F. of which was less than the other by I part in IO,000, as shown by the maker's certificates, and also by a direct comparison at the time they were used. Hence the E.M.F. of this cell is taken as I.0192 volts.

The standard half-ohm coil, M, is of the Reichsanstalt form as made by Leeds & Co., and was made with special reference to carrying currents as great as two amperes. It is provided with both current and potential terminals, the half ohm being the resistance between the two points where the potential terminals are attached. A. W. SMITH.

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The exact value of this resistance was determined by the National Bureau of Standards and was found to be 0.50008 ohm at  $20^{\circ}$  C. in terms of the mean values of two coils which were redetermined at the Reichsanstalt in July, 1902.

As shown in the figure, the current terminals are joined in series with the heating coil, and the potential terminals are joined to one side of the double pole, double throw switch, T. When this switch is closed the difference of potential between the terminals of the standard half ohm is balanced against the E.M.F. of whichever standard cell is in circuit, the difference, if any, being indicated by the galvanometer on closing the key K. The main current through C and M is continually adjusted to keep the galvanometer deflection zero. The observer sat with his eye at the telescope watching the galvanometer deflections, while one hand continually tapped the key K, and the other varied the resistance R by whatever amount was necessary to maintain zero deflection.

In order to be protected as far as possible from fluctuations in temperature, the standard cells and resistance were placed in a wooden box and covered with cotton wool. This box occupied a position on the table, found by trial, such that the heat from the register and the cold from the window balanced to give a nearly constant temperature of about 20° C. Quite large fluctuations in the temperature of the room, if not continued too long, produced very little change within the box.

Measurement of Current. — As explained above, the current through the heating coil was maintained constant by keeping the galvanometer deflection as near zero as possible. The deflections to one side or the other were usually less than I or 2 mm., and the corresponding steady deflections, had they been observed, would have been considerably less. As the deflections were as often one way as the other, the too small current at one time would tend to balance the too large current of another, thus making the

Knowing the resistance of the standard coil M, and the difference of potential between its terminals, the current it carries is readily calculated by Ohm's law. The current in the heating coil C is equal to that in M, less the small portion which flows through the potentiometer circuit PQ.

Measurement of E.M.F. - The difference of potential between the terminals of the heating coil was measured by the usual potentiometer method as shown in Fig. 3. Q is a fixed resistance of 10,000 ohms, while P is about 1,100 ohms. Both resistances in series are joined in parallel with the heating coil and thus are subjected to a total fall of potential of about ten volts, of which a little over one volt is in the part P. As shown in the diagram, two lead wires from the terminals of P run to the switch T. On throwing the switch to this side, the fall of potential in P is compared against the E.M.F. of the same standard cell used for the measurement of cur-The resistance of P is varied to give zero deflection of the rent. galvanometer. Then, if E is the E.M.F. of the standard cell and Pis the resistance corresponding to zero deflection of the galvanometer, the difference of potential, V, measured by the potentiometer is given by the expression

$$V = E \frac{Q+P}{P}.$$

When running an experiment, the switch T was kept closed on the current side in order to see that the latter remained constant. When everything was going smoothly, the switch was quickly thrown to the other side — the direction of the galvanometer deflection noted — and then thrown back again. The smallest change in P corresponded to a deflection of eight scale divisions, and when it was not possible to adjust P to give zero deflection, the small deflection was observed and the value of P corrected accordingly.

The temperature of the potentiometer coils, or at least that outside of the boxes which contained them, was about  $20^{\circ}$  C. in all of the experiments here reported. As it is the ratio of the resistances of these coils that is used in the measurement of E.M.F., any small change in temperature would affect this ratio very much less than it would the absolute value of the resistances. In fact it would be proportional to the difference between the temperature coefficients of the two portions of the total resistance and is therefore inappreciable for a variation of one or two degrees, or even more.

Measurement of Time. — This was measured by an Elgin watch which was losing less than thirty seconds a month. The seconds hand was viewed with a small reading glass which magnified five diameters, and just as the 30-seconds mark was covered by the hand, the switch S was closed, thus starting the current through the coil C at the beginning of the 31st second. When it was desired to stop the current the same procedure was repeated. Whenever the length of time was arbitrary and would allow it, the current was allowed to flow an integral number of minutes, so that the seconds hand of the watch could be read in the same position at both the starting and the stopping of the current.

In order to obtain some idea of the accuracy with which intervals of time could be measured by this method, twelve single minute intervals as observed with the watch were recorded upon a chronograph sheet which was also receiving the records of seconds from the astronomical clock.

The duration of these intervals as obtained from the chronograph are given below.

60.22	60.15	60.15
60.23	60.22	60.25
60.15	60.15	60.10
60.20	60.15	60.15
	11 = 60.177, prob. error r minute = 60.165 sider	

The calculated probable error of one observation is 0.03 sec. and the greatest actual difference of a single observation from the mean is 0.08 second. From this it appears that intervals of time measured with the watch can be depended upon to at least a tenth of a second, and they probably possess a much greater accuracy.

The Thermometer. — The thermometer used in these experiments was one made to order by H. J. Green, of Brooklyn, N. Y. It was graduated on the stem to hundredths of degrees from  $- 13^{\circ}$  C. to  $+ 1^{\circ}.6$  C. Its entire length was 95 cm. and it was 6 mm. in

aid of a small reading glass the temperature could easily be read to thousandths of a degree.

The zero of this thermometer was too low by  $0^{\circ}.035$ , that is, the temperature of melting ice gave the reading  $+ 0^{\circ}.035$  C. This difference is doubtless due in part to the fact that the stem was exposed to the temperature of the room (about  $20^{\circ}$  C.), but as this was the same in the actual experiments and when the "zero point" was determined no error is introduced by not applying the stem correction. The "zero point" was determined before and during the experiments by three different methods, viz., by placing the bulb and several centimeters of the stem into a mixture of clear ice and pure distilled water; by plunging it into freshly fallen snow which was saturated with pure distilled water; and by placing it in pure distilled water which was being frozen in a large test-tube. Each of these methods gave the reading  $+ 0^{\circ}.035$  C. as the true zero, and all readings of the thermometer are corrected by this amount.

The brass case of the thermometer was kept standing in the ice surrounding the chamber D, and when not in use the thermometer was always within this case and at a temperature not higher than two or three tenths of a degree above zero. During the entire series of experiments here reported the thermometer was not allowed to rise above  $+ 2^{\circ}$  C. and the lowest temperatures to which it was subjected rarely exceeded  $- 5^{\circ}$  C.

Manipulation of the Ice. — The ice used in these experiments was very carefully selected, only that which was perfectly clear and transparent and free from bubbles being taken. The structure of all the ice used, both the commercial ice and that made from pure distilled water, was decidedly crystalline, the axis of the crystals being normal to the surface at which the ice was formed. A piece of ice which externally appeared the same in all directions quickly revealed its crystalline nature when the attempt was made to split it. If the edge of a sharp knife was pressed againt the ice to divide it along the axis of crystallization, it readily separated along an almost perfect plane. The same is true of the planes at right angles to the axis, provided it is not too near the end of the crystals. In any other direction, and even that perpendicular to the axis if too near the end of the crystals, the pressure of the knife resulted in merely shattering the ice as though it were a bundle of glass tubes. By cleaving the ice in planes at right angles and parallel to the axis of crystallization it is possible, however, to divide it into small cubes with smooth surfaces, each one of which was as clear as the original piece.

As the weather was seldom cold enough to keep the ice from melting, about a hundred grams of these pieces were dropped into a beaker surrounded by a freezing mixture. To prevent their freezing to the sides of the beaker a few pieces were introduced at a time and constantly stirred until they were cooled below  $0^{\circ}$  C. and whatever free water there might have been on the surface was completely frozen. The beaker was then closed with a ball of cotton wool to prevent the warmer air from coming in contact with the ice, and left in the freezing mixture some minutes longer.

In the meanwhile the proper amount of oil was measured out into a flask, weighed and placed in a freezing mixture, where it was cooled to about  $-6^{\circ}$  C. This flask was now removed, and the oil quickly poured into the calorimeter through the special funnel. Both the flask and the funnel were then laid aside to assume the temperature of the room, when they were reweighed to determine just how much oil entered the calorimeter.

In order to weigh the ice without its melting the beaker containing it is removed from the freezing mixture, quickly wiped dry, wrapped with cotton and placed within a larger beaker, the whole being covered with a papier mâché cap. This arrangement was placed on the balance and weighed. It is then carried to the calorimeter, the cover and ball of cotton removed, and the ice poured through the brass tube into the cold oil below. The ice is directed into this tube by a funnel formed of filter paper. At no time was the appearance of the ice such as to indicate that any portion was melting, nor was any water ever caught by the filter paper as the ice passed over it. The fall of the ice was broken by striking the stirrer and thus splashing of the oil was prevented. Usually the ice was in the oil of the calorimeter within three minutes after it was taken form the forming minimum state of the calorimeter within three minutes after No. 4.]

HEAT OF FUSION OF ICE.

rimeter the beaker was closed with the cotton ball, the cover replaced and the whole immediately weighed, thus determining the amount of ice employed.

If the equilibrium temperature of the oil, ice and calorimeter was much below  $-2^{\circ}$  C. or  $-2^{\circ}.5$  C., it was cautiously raised to this point and then left for an hour, during which time it slowly rose some tenths of a degree further. At this point readings of temperature were commenced, while the oil and ice were constantly stirred at a uniform rate. By alternate periods of warming due to radiation alone with periods in which the rate of warming is increased by an electric current through the coil, the relation between change of temperature and joules was obtained, as already explained.

When the temperature reached  $-1^{\circ}$  C., or thereabouts, the larger current was applied for a sufficient time (as determined by previous calculation) to melt the ice. During this time one observer constantly watched the galvanometer and maintained the current constant, while the other continued the stirring and read the thermometer each minute. These readings were utilized in the calculation of the heat lost by radiation during the experiment.

After the experiment was concluded the calorimeter with the oil and water was again weighed to furnish a check upon the weight of ice used. This weight was always within a few centigrams of the sum of the weights of the separate portions.

## Sources of Error.

The various sources of error in this method are :

1. Heat lost by radiation, conduction, convection, etc.

2. Heat produced by stirring.

3. Electrolysis of the water.

4. Loss of heat by evaporation.

5. Use of the thermometer.

Under the first head it must be noticed that the temperature of

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prove that the loss of heat did thus depend upon the temperature of the calorimeter at the time, and not upon previous temperatures, two determinations of the heat lost at a given temperature were made. In one this temperature was reached by adding some very cold oil, after which the rate of cooling was observed for a considerable time. Again this temperature was reached by quickly warming the oil several degrees by the electric current. The rate of cooling, after the first few minutes, was identical with the former, thus showing that it depended solely upon the temperature at the moment.

The loss of heat by convection air currents is reduced to a minimum by filling the space around the calorimeter with cotton wool.

Whatever heat may be conducted to the calorimeter from the outside by the wires conveying the current is included in the determination of the heat lost by radiation, etc. However this is very small, since these four wires are of No. 16 copper wire, and the heat would have to be conducted a distance of 30 cm. and through air at 0° C. The heat generated in these wires by the current is about one joule during each experiment and is, therefore, inappreciable.

It thus appears that the loss or gain of heat due to these causes is a definite quantity capable of being determined. As this determination is based upon measurements made just before and just after the main experiment, the total error introduced cannot exceed a few joules.

Heat Produced by Stirring. — By extremely vigorous stirring it was possible to produce enough heat to cause an observable effect upon the rate of cooling due to radiation, etc. As ordinarily used, however, the stirrer was raised and lowered about 3 cm. fifty or sixty times a minute. At this rate no different effect could be observed from that when the stirring was only four times per minute. The heating must, therefore, be very small, and whatever it is is

No. 4.]

be present later as the coil is well coated with shellac, wetted with kerosene oil, and only a small portion of one end is ever below the surface of the water.

Loss of Heat by Evaporation. — In the usual method of mixtures there is always a considerable amount of evaporation from the surface of the water, and a consequent loss of heat. In these experiments, however, the water is covered by the oil and there is no evaporation. The oil itself evaporates exceedingly slowly, and whatever heat is thus used is included in the determination of the loss by radiation, etc.

Use of the Thermometer. — The thermometer was used to measure the initial and final temperatures for determining the amounts of the corrections to be applied. As this is a very good standard thermometer recently made by Green, it is very improbable that there is any appreciable error in the length of that portion of the scale here used. The greatest error is introduced in the assumption that the temperature indicated by the thermometer truly represents the temperature of all portions of the calorimeter. As these readings were taken only when the temperature was changing very slowly and while the contents of the calorimeter were thoroughly stirred, this assumption can not be very far from the truth.

## WEIGHTING OF THE EXPERIMENTS.

Each of the eight experiments here reported was conducted with the greatest care, and there is no reason for discrediting the result of any one of them. Nevertheless there are certain circumstances to be noted which warrant greater confidence in some experiments than in others, and these considerations are taken into account by the following system of weighting.

The maximum weight given to any experiment is 6, made up as follows :

One point if there has been a direct determination of heat capacity with ice preceding the regular experiment of melting the ice.

One point if the regular experiment has been followed by a direct determination of heat capacity with water.

Two points for a short duration of the experiment, that is, less than forty minutes.

One point if all the ice is melted with a single application of the current.

One point if the rate of cooling at the end of the experiment is definite and constant.

## PRELIMINARY EXPERIMENTS.

The first experiments were made using the clearest portions of the artificial ice furnished to the laboratory. It was intended to use this ice for the preliminary work and later to try some ice frozen from the purest water obtainable. It was expected from the statements of some of the earlier investigators along this line, especially the paper by Person, that the specific heat of ice would increase gradually with increase of temperature from its value at  $-2^{\circ}$  C., and lower temperatures, and possibly approach the value for water as 0° C. was reached. In determining the heat capacity of the combined apparatus with ice for temperatures approaching 0° C., this idea seemed to be corroborated by experiment. A great many experiments were made to determine the exact value of this increased heat capacity. At first all determinations were for temperatures below - 0°.5 C., and the increased heat capacity of the ice did not exceed that of water. Later, when the range from  $-0^{\circ}$ .5 C. to  $0^{\circ}$  C. was studied the heat capacity came out as being inversely proportional to the temperature below 0° C., increasing without limit as 0° C. was approached ! This at once raised suspicions that something was wrong, and further investigation showed that there had been some melting of the ice. When the temperature of the oil and ice was already very near to 0° C. it is probable that the current, though very small, raised the temperature of some portions of the oil to such a temperature that local melting of the ice was possible. Whatever water was detached from the ice and remained in the oil in small drops, would not freeze again when the equilibrium temperature was reached. However it was never possible to find sufficient water to account for all of the heat absorbed, and doubtless the remainder was used in internal melting. As shown below, unless the ice is absolutely pure throughout, those portions containing the greatest amount of impurities will melt first and at the lowest temperatures. As the temperature is raised a

No. 4.]

greater and greater amount of the impure ice will reach its melting point, requiring an ever-increasing amount of heat to produce a given change in temperature. The water from this melting could remain on the surface of the ice, or if the melting was internal it would remain in its own cavity. Although in contact with the ice this water (or rather solution) could not be expected to freeze again and return its heat of fusion to the oil, even though the equilibrium temperature was two or three tenths of a degree below o<sup>o</sup> C.

Moreover, at this time the entire question was complicated by the possibility that the oil might have some action upon the ice. This hardly seemed probable from the nature of the substances, and the fact that other investigators have observed no action upon ice when placed in refined kerosene. It is proved below that there is no such action.

Specific Heat of Ice. - There was now an imperative demand that the specific heat of ice be carefully studied over the range of temperature from - 1° C. to 0° C. Ordinary distilled water was placed in a large test-tube with a smaller test-tube suspended in the center. The water was frozen from the bottom up, thus forming a cylinder of ice between the two test-tubes, about 7 mm. in thickness and as many centimeters in height. A new heating coil was arranged at the bottom of the calorimeter and occupying only about I cm. in depth. Over this was placed the test-tube containing the ice. Any possible action of the oil upon the ice was now entirely eliminated as they were separated by the glass wall of the test-tube. Heat was slowly applied by the small current through the coil, and the heat capacity of the ice determined as before. Although much less than before, yet at  $-0^{\circ}.2$  C., it appeared as great as for water and at  $-0^{\circ}$ . I C. it was twice as great. On removing the tube and closely examining it, a bit of water was seen at the point where the last ice was formed. Doubtless this drop contained the greater part of whatever impurities existed in the tube of water and being the last to freeze it was the first to melt.

After this only the purest water was used for making ice. Such water was obtained from Dr. H. C. Jones, who kindly furnished all that was needed. This water was prepared by distilling ordinary distilled water from a solution of chromic acid, the vapor being then passed directly into a boiling solution of barium hydroxide to remove all traces of carbonic acid. The vapor was then condensed in a block tin condenser and collected in a glass bottle. The latter was previously treated with boiling hydrochloric acid for a long time in order to render the glass insoluble in water. This water was being continually distilled for use in conductivity experiments in the Physical Chemical Laboratory, and possessed a specific resistance of one megohm.

A portion of this water was thoroughly boiled to remove the dissolved air and the test-tube filled to the desired height. The inner tube was not used, but a layer of ice was frozen on the sides of the tube to about the same thickness as before, the residual water in the center being thrown out. The ice thus formed is very pure, whatever impurities there might have been in the water at the beginning being thrown out in the residual water. Two such tubes were prepared and placed in the calorimeter, which was previously filled with cold oil.

Observations were made for the determination of heat capacity, the same as in a regular experiment and already described. The same experiment was repeated the following day (Feb. 20). The effect of having the oil in contact with the ice was determined by filling the cavity in the center of the ice tubes with oil, and again taking a series of observations for heat capacity. Any melting of the ice by the oil would be manifest by the increased amount of heat required to produce a given rise in temperature.

The results of these determinations are summarized in the following table. The second column gives the temperature at which the determination was made, the thermometer reading being corrected for zero point. The numbers in the third column give the change in temperature due to the current. In order to render these more comparable, each one is divided by the time (in minutes) that the current was flowing. The results are given in the fourth column and express the change in temperature produced by the current flowing for one minute. Since the current was precisely the same for each determination, the constancy of these numbers shows the constancy of the heat capacity of the calorimeter and its contents, for temperatures ranging from  $-1^{\circ}.4$  C. right up to practically No. 4.]

 $o^{\circ}$  C. In the determinations made with the oil in contact with the ice, this constancy was as marked, if not more so, showing that even in this case there was no melting of the ice below  $o^{\circ}$  C.

Neither is there any increase in the specific heat of ice as it approaches  $0^{\circ}$  C., as has been maintained by some investigators, but it remains a definite constant right up to the point at which the ice melts. That is, such is the case for this very pure ice, as is shown by the constancy of its heat capacity, and this is what would be expected since ice is a crystalline substance. As already pointed out, if there are impurities in the ice, even in very small amounts, an apparent increase in its specific heat may be produced by the lowering of the melting point of some portions of the ice.

TABLE	II.
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Date.	Actual Temp.	Change in Temp.	Change in Temp. per Min.	
Feb. 19.	- 0.48	.161	.0322	
	-0.24	.065	.0325	
	- 0.36	.064	.0320	
Feb. 20.	- 1.43	.160	.0320	With ice mantles
	- 1.03	:161	.0322	
	- 0.73	.163	.0326	in glass test-tube
	- 0.23	.163	.0326	
	- 0.09	.133	.0332	
	- 0.02	.063	.0315	
Feb. 20.	- 0.92	.160	.0320 •	Ice mantles filled
	- 0.66	.160	.0320	with kerosene.
	- 0.23	.160	.0320	

Heat Capacity of Ice.

Effect of Mixing Water and Oil. — When the ice melts the resulting water is stirred up with the oil, and the question arises whether this mixture of the two liquids is accompanied by any thermal change. The point was subjected to experiment in the following way. About 300 c.c. of oil was placed in the calorimeter, and about 50 c.c. of water, the latter being in a large test-tube. A

taken to make sure that the temperature was constant while the oil was thoroughly stirred. Then the test-tube was broken and the water allowed to flow out and mingle with the oil, and there appeared to be a rise in temperature of  $0^{\circ}.001$  C. In order to see whether this was due to any action between the oil and water, or only to the mechanical energy put forth in breaking the tube, the motion of breaking the test-tube was repeated. In this case also there was a rise of temperature of the same amount as before, and since this time there was no question of water mixing with the oil, this increase in temperature, if real, must be due to the mechanical energy expended in the process of breaking the tube.

It is certainly safe to assert that there is no production or absorption of heat when the oil and water are stirred up together.

## EXPERIMENTS WITH PURE ICE.

In view of the preceding investigations, all further experiments were made with ice formed from the pure distilled water. About half a liter of this water was boiled for twenty or thirty minutes to remove as much of the dissolved air as possible. The remaining 300 c.c. of water was poured into a beaker which it nearly filled, and when cooled somewhat the beaker was set in a freezing mixture of fine ice and salt. If supercooling of the water was allowed, ice crystals would suddenly form throughout the water. To prevent this form of ice and obtain it in a firm compact layer a small bit of ice was frozen to the side of the beaker just above the surface of the water, and below the surface of the freezing mixture outside. Here it would remain till the outer layer of water was cold enough to freeze. Then a film of ice was seen to start from the bit on the glass and spread over the inner surface of the beaker. After an hour or two this layer of ice reached a thickness of nearly a centimeter. The remaining water was discarded and the ice removed from the beaker by slightly warming the outside. This cup of ice was taken to the coldest place available and cut into cubes ranging from one to one fourth cubic centimeter in size. These pieces were dropped into another beaker in a freezing mixture where they were cooled several degrees below 0° C. and thus freed from any clinging water either on the surface or interior. The ice was then weighed and quickly transferred to the calorimeter as already described.

Eight determinations of the heat of fusion of this ice were made on as many different days, one entire day being required to make one determination. During the greater part of this period the weather was below 0° C. in the morning which greatly facilitated the handling and weighing of the ice.

The amounts of ice used in each of these experiments are shown in the following table :

Date.	Weight of Ice.					
2000.	Beaker + Ice.	Beaker.	Ice.			
Feb. 27.	287.86	186.49	101.37			
Feb. 28.	292.78	190.43	102.35			
Mar. 2.	274.82	194.59	80.23			
Mar. 3.	283.12	194.67	88.45			
Mar. 4.	307.43	1 <b>94</b> .41	113.02			
Mar. 5.	289.91	198.84	91.07			
Mar. 6.	302.37	200.09	102.28			
Mar. 7.	275.73	189.81	85.92			

 TABLE III.

 Amounts of ice used in the experiments.

Determination of Heat Capacity. — With this very pure ice which it had been shown could be warmed right up to  $0^{\circ}$  C. without any melting or apparent increase of its specific heat, it was expected that the initial temperature could safely be brought to within a few tenths of a degree of  $0^{\circ}$  C. Nevertheless there appeared unmistakable evidences that if the temperature was too near  $0^{\circ}$  C. a small amount of melting of the ice would be caused by the current used in the preliminary experiments to determine the heat capacity of the calorimeter with the ice. Such determinations were, therefore, made only at temperatures below  $-1^{\circ}$  C.

In the determination of the heat capacity, the current, as already stated, was that which would flow through the heating coil when its terminals were maintained at a difference of potential equal to the E.M.F., E, of one standard cell. The heat produced is then given by the formula  $E^{2t}/R$ , where R is the resistance of the coil and tthe number of seconds that the current was flowing. The ratio of the heat generated by the current, expressed in joules, to the change in temperature which it produced is termed the "heat capacity with ice."

The results of these determinations are given in Table IV. The mean temperature of the calorimeter and contents during each determination of heat capacity with ice is given in the second column. The third column shows the change in temperature produced by the amount of heat recorded in the fourth column. Often two or more determinations were made with the same ice at slightly different temperatures, the average of the results being used in the calculation of heat capacity, which is given in the fifth column in terms of the number of joules which would be required to raise the calorimeter and contents one degree.

The initial equilibrium temperature of the experiment for March 3 was too near 0° C. to allow a direct determination of heat capacity. Of course this could not be very different from the heat capacity on previous days as the same calorimeter and the same amount of oil was used each time, and approximately the same amount of ice. The determinations of February 27, February 28 and March 2 were all very satisfactory, and these are plotted as ordinates against the corresponding amounts of ice as abscissæ, and for the short range required of this curve it gives the heat capacity with ice for the experiments of March 3, 4 and 7 are obtained, then, from the determinations of the first three experiments by means of this curve.

The second part of Table IV. contains similar data for the heat capacity with water, obtained after the ice has been melted. A direct determination was made each day save the last, when the final equilibrium temperature was at the upper limit of the thermometer and higher temperatures could not be measured. The amount of ice used on this day was a mean between the amounts used on March 2 and 3, and as the same amount of oil was used, the heat capacity must be very closely the mean of the values obtained on these two days, and this mean is taken for the heat capacity.

Management of the Floctwice Fuerow The details of the

### TABLE IV.

		Wit	h Ice.			With	Water.	
Date.	Temp.	Change in Temp.	Joules.	Joules per Degree.	Temp.	Change in Temp.	Joules.	Joules per Degree
Feb. 27	-1.40	.096			+.83	.140		1
	i <b>-1.09</b>	.097	62.75	650	+.86	.140	125.5	896
Feb. 28	-1.60	.194	1					1
	1 -1.12	.193	125.5	648	+.95	.744	660.	887
Mar. 2	-2.00	.198		1				
	-1.54	.198	ł.	1	+.25	.152	125.5	
	-1.16	.198	125.5	634	+.40	.304	251.0	825
Mar. 3	Ì	from curv	e	640	+.22	.149		
	1	1	l		+.34	.150	125.5	839
Mar. 4		"	6	656	+.67	.705	660	935
Mar. 5	-0.60	.147	125.5	853	+.49	.609	618	1016
Mar. 6	-1.10	.142	1	890				1
	-0.74	.141	125.5	638	+.87	.299	309	1034
Mar. 7	1	from curve	e	i	Mean	of Mar. 2	and 3.	832

Heat Capacity.

NOTE.—The amount of oil used on March 5 and 6 was 300 c.c. Hence the heat capacity is greater on these days than on the others when only 200 c.c. of oil was used.

values of the E.M.F. of the cell and the resistance of the coil, given in the third and fourth column, are those determined by the National Bureau of Standards. The value of the current thus determined is given in the fifth column.

The National Bureau of Standards also determined the value of the resistances Q and P, which were used as a potentiometer for the measurement of the E.M.F. between the terminals of the heating Q was a box marked 10,000 ohms, while P was another box coil. in which the resistance could be varied by one-ohm steps. The resistances used were nominally 1,113 ohms and 1,114 ohms, being that value which gave the nearest balance, the difference from a complete balance being measured by the deflection of the galvanom-The mean deflection for each experiment is given in the eter. eighth column, and the corresponding change in P necessary to give zero deflection is given in the ninth column. The voltage thus measured by the potentiometer is given the tenth column. The current through the heating coil is obtained by subtracting that in the potentiometer circuit from the total measured in the standard coil. The last column gives the amount of heat generated in the

		Measuren	Measurement of Current.	at.		-	Measuremei	Measurement of Voltage.	ė		Time	
Date.	No. of	E.M.F. of Cell.	Resistance of Coil.	Current.	Potenti Resist	Potentiometer Resistanccs.	Mean Gal- vanometer	Mean Gal- Equivalent vanometer Resistance	Voltage 2+P+	Potentiome- ter Current	Current was Flowing.	E(I-i)t.
		•	•		ð	ď	Denection.	r=d+8.	P+r	$i = \overline{Q + P}$	•	
eb. 2	1 329	1.0193	0.50008	2.03736	9949.7	1,114.82	-1.00	-0.12	10.1175	0.00091	1,710	35,248
	" 78	3	z	÷	2	1,113.79	0	0	10.1249	2	3	35,278
Mar.	; 5	2	2	2	2	1,114.82	-0.37	-0.0	10.1168	2	1,335	27,768
ar.	3 3	3	2	3	2	3	-1.62	0.20	10.1181	;	1,460	30,210
ar.	4	3	3	3	3	"	-0.5 <u>5</u>	10.0	10.1170	:	1,865	38,441
ar.	5 328	1.0192	2	2.03716	"	1,113.79	+3.60	+0.45	10.1202	2	1,510	31,131
ar.	6 329	1.0193	z	2.03736	3	1,114.82	-1.83	-0.23	10.1174	3	1,725	35,560
ar.	7 328	1.0192	*	2.03716	2	*	-1.90	-0.24	10.1175	2	1.465	30,195

TABLE V. Measurement of the Electrical Energy.

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heating coil, being the continued product of the E.M.F., current and time.

That portion of this heat which was used in other ways than melting ice is calculated in Table VI. The second column gives the equilibrium temperature of the calorimeter and its contents just before the current was passed. This, multiplied by the heat capacity from Table IV., gives the heat required to raise the whole to  $o^{\circ}$  C., and is termed the "initial correction." The "final correction" is calculated in the same way, being the heat required to raise the calorimeter with water from  $o^{\circ}$  C. to the final temperature.

The heat lost (or gained) to the calorimeter by the combined action of radiation, conduction, convection, stirring, etc., is determined by the rate of cooling (or warming) experienced when no heat is being supplied by the current. These rates were observed and recorded in connection with the determinations of heat capacity. Expressed in joules per minute, they are plotted as ordinates against

Date.	Initial Temperature.	Heat Capacity with Ice.	Initial Correction.	Finel Temperature.	Heat Capacity with Water.	Final Correction.	Average Temperature.	Radiation per Minute.	Duration of Experiment.	Correction for Radiation, etc.	Total Correction.
Feb. 27	788	650	512	+ .852	896	763	+.51	2.45	37	91	1366
Feb. 28	687	648	445	+ .642	887	569	+.41	2.10	33	69	1083
Mar. 2	987	634	626	+ .165	825	136	+.61	2.50	61	153	915
Mar. 3	709	640	454	+ .124	839	104	+.41	1.50	55	83	641
Mar. 4	535	656	351	+ .332	935	310	+.52	2.00	39	78	739
Mar. 5	468	853	<b>399</b> <sup>1</sup>	+ .173	1016	176	+.61	2.20	37	81	656
Mar. 6	605	890	538	+ .693	1034	716	+.68	4.00	33	132	1386
Mar. 7	389	638	248	+1.298	832	1080	+.80	4.00	. 40	160	1488

TABLE	VI.
Correctio	ns.

the corresponding temperatures as abscissæ, and the resulting curve gives the loss at any temperature. The eighth column gives the average temperature of the calorimeter during each experiment, and the loss of heat by radiation, etc., at this temperature is read from the curve corresponding to that experiment and recorded in the ninth column. The loss of heat at a given temperature is not necessarily the same on different days, since the temperature of the chamber D, Fig. 2, might have varied by several tenths of a degree.

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The "duration" of the experiment is the interval in minutes between the reading of the initial and final temperatures and during which time the loss of heat is effective in reducing the value of the latter. The product of the loss of heat per minute by the duration gives the total amount of heat lost through these causes. The total correction given in the last column is the sum of these three corrections and represents that portion of the heat generated by the current which is not used in melting ice.

#### SUMMARY.

In the following table is given the final calculations for the heat of fusion. The numbers in the second and third columns are taken from Tables V. and VI., their difference being given in the fourth column. This is the amount of heat used in melting the quantity of ice in the fifth column, and the amount of heat per gram of ice is given in the sixth column. The last column shows the weight given to each experiment:

	Ta	BLE	VII.
--	----	-----	------

Date.	Total Joules.	Total Cor.	Cor. Joules.	Weight of Ice.	Heat of Fusion.	Weight- ing.
Feb. 27	35,248	1,366	33,882	101.37	334.24	6
Feb. 28	35,278	1,083	34,191	102.35	334.06	5
Mar. 2	27,768	915	26,848	80.23	334.69	3
Mar. 3	30,210	641	29,569	88.45	334.30	2
Mar. 4	38,441	739	37,702	113.02	333.59	4
Mar. 5	31,131	656	30,475	91.07	334.63	5
Mar. 6	35,560	1,386	34,174	102.28	334.12	5
Mar. 7	30,195	1,488	28,707	85.92	334.12	3
			Weigl	hted mean =	334.21	1
		Probable of	error of	• • • =	.08	

Summary of Results.

All of the determinations of the heat of fusion are seen to agree

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No. 4.]

The probable error of the weighted mean, calculated by the method of least squares, is 0.08 joule, thus giving for the final value of the heat of fusion of ice

 $334.21 \pm 0.08$  joules,

taking the value of the Clark cell as 1.434 volts at 15° C.

If there is an error of I part in 1,000 in the value of the Clark cell, it would alter this value of the heat of fusion of ice by 2 parts in 1,000, since the electrical energy has been calculated from the formula EIt, and both E and I are determined in terms of the standard cell, the E.M.F. of which is expressed in terms of the Clark cell.

This result can be expressed in terms of mean calories if we take the value for a mean calorie to be 4.1832 joules, as determined by Reynolds and Moorby,<sup>1</sup> and recently corroborated by Barnes.<sup>2</sup> This gives for the heat of fusion of ice

## 79.896 mean calories.

Since the number 80 is familiarly used to express the heat of fusion of ice, it is interesting to note that  $334.21 \div 80 = 4.1776$  joules, which is very closely the minimum specific heat of water as determined by Barnes. In other words, the heat of fusion of ice at 0° C. is

80.00 "calories at 37° C."

This value for the heat of fusion of ice is somewhat lower than that obtained by Hess, which appears the most trustworthy of previous determinations. However Hess stands alone in finding a value greater than 80 mean calories, or 336 joules, while the value here obtained is near the mean of all the previous determinations. It would be interesting to compare the heats of fusion of samples of ice prepared by different methods and of various degrees of purity. Some of the preliminary experiments with commercial ice seemed to indicate a slightly less heat of fusion, but these experiments will not warrant a more definite statement. However, for this very

<sup>&</sup>lt;sup>1</sup>Reynolds and Moorby, Phil. Trans., Vol. 190, p. 381, 1897.

<sup>&</sup>lt;sup>2</sup> Barnes, Phil. Trans., Vol. 199, p. 149, 1902.

pure ice, made as specified above, the value 334.21 joules in terms of the Clark at 1.434 volts at 15° C. will stand.

The writer's thanks are extended to Professor Ames for his interest and many helpful suggestions throughout this investigation. Valuable assistance has also been rendered by Mrs. Smith in that part of the work which required two observers.

JOHNS HOPKINS UNIVERSITY, June 1, 1903.



# THE CORONAL METHOD OF ESTIMATING ATMOSPHERIC NUCLEATION.

#### BY CARL BARUS.

I. Introductory. — With the advent of spring the values of atmospheric nucleation, if laid off on the same scale as in my earlier papers, have returned to the low order of values found last fall and the details of the temperature effect are obscured. I have supposed from this that temperatures below freezing are particularly favorable to high nucleation. One may note, moreover, that the distribution of atmospheric electrical potential is a maximum in winter and falls off in its yearly period in a way similar to the observed nucleation. The frequent occurrence of day minima in both cases should also be noticed.

The presence of maximum nucleation during the winter months when the maximum of dust contents is certainly to be anticipated for the summer, together with the fact that the numbers of nuclei found by the coronal method is much lower than the usual order of Aitken's<sup>1</sup> data, is worthy of remark. To produce coronas the nuclei must be very closely of the same size; for in a large trough, a rigorous uniformity of diameter of fog particle and possibly of distribution is implied, if the corona produced is to be sharp and brilliant. Particles of even slightly different sizes would give a blurred effect or a mere fog. Hence, as I understand it, the effect of ordinary dust vanishes from the corona and the nucleation observed is probably something much more definite. It is for this reason that in spite of very discouraging drawbacks, my interest in the subject has not waned, though I am well aware that the effect of chemical products of combustion in winter, such as sulphuric acid and the sulphides, has not been eliminated.

The subject as a whole has received enhanced interest in view of its relation to Arrhenius's interpretation of the geophysical impor-

<sup>1</sup> In the country after rain, 32,000; clear, 130,000; in cities, 100,000 to 500,000, etc. These data are about five times larger than the coronal values.

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tance of cosmical, and in particular of solar dust. Some limitation has been put on the light-pressure theory by Schwarzschild, but this has rather stimulated Arrhenius to give a sharper expression to his views, and the theory now appears as the central figure of an elaborate treatise of cosmical physics.<sup>1</sup>

I have hoped therefore by aid of the present method eventually to add a contribution of my own. I have now nearly a complete record of the fall, winter and spring nucleations, though some of the early data will have to be repeated. There remain for completion the midsummer nucleations, which will be added in due time.

2. Apparatus.—This consists (Fig. 1) of a rectangular box, AA, 50 cm. long, 10 cm. in thickness and 10 cm. or preferably less in height, made of some material impervious to water. Wood covered while warm with a thick coating of wax and Burgundy pitch answers the purpose very well and is much lighter than (rigid) metallic vessels. The front and rear faces of the box are of thick plate glass. This must be kept clean on the inside and suitable scrapers with a vertical straight edge of soft rubber movable to and fro along the glass by aid of a long horizontal rod should be provided within the box. The rods pass out through perforated corks in the tubes e, with additional protection to secure an air-tight joint when not in use.

The air within the box communicates with the outside by three or more stopcocks, of which B is very wide ( $\frac{1}{2}$  inch or more) in order that sudden exhaustion may be made through it. The stopcock, C, communicates with the atmosphere at a place free from local nucleation, through a length of  $\frac{1}{4}$ -inch lead pipe; C furthermore communicates with the interior of the box through a flat coil, P, of the same lead pipe, lying in the bottom of the trough, below the water level, ww. A coil of lead pipe in a water-bath may also be inserted on the outside of the box, the object being to heat the air to room temperature, especially in winter. Two thermometers, T. T', with their bulbs respectively in the air and the water within the

double layer of cotton cloth, nn, supported on a framework of stout copper wire. The trough should be mounted with its longitudinal axis on trunnions (not shown) in order that the whole interior may be moistened by a single rotation. The stopcock, F, provided with a cotton filter is often useful in testing.

The horizontal diameter of the coronas is observed, the point source of light being two meters off on one side and a suitable goniometer about one meter on the other side of the trough.

An ordinary jet pump suffices for aspiration (with the cocks C and B open), and with an added vacuum chamber provided with a

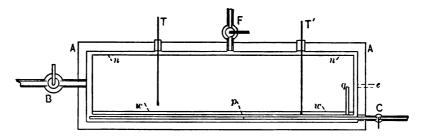


Fig. 1.

vacuum or mercury gauge, for sudden exhaustion (C and B having been closed), care being taken that the connecting tubing beyond B is wide.

3. Diffusion from Two Surfaces. — The high values of nucleation observed during the winter months will not be received without misgiving, since the air during the very cold weather is nearly dry and after being heated to  $20^{\circ}$  very far from saturation. Deficient saturation, however, would decrease the size of the fog particles and, *cæteris paribus*, increase the size of the coronas, in this way showing the same result as excessive nucleation. Hence it is necessary to estimate the time which is needed to saturate dry air in the apparatus described above.

Given a rectangular trough at the bottom of which is a surface of water and at the top of which a surface of saturated sloth the the surface of the water or a - x below the wet cloth, at the time t,

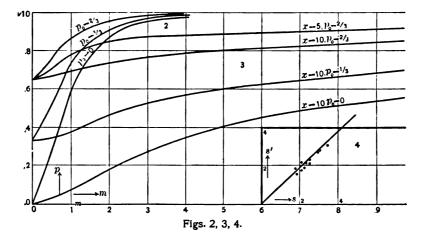
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$$p = I - \frac{4}{\pi} \left( \sin \frac{\pi x}{a} e^{-(\pi/a)^2 kt} + \frac{1}{8} \sin \frac{3\pi x}{a} e^{-(3\pi/a)^2 kt} + \cdots \right)$$

where k is the coefficient of diffusion.

If diffusion takes place into a partially saturated atmosphere at an initial pressure  $p_0$  the factor  $4/\pi$  in the last equation is to be replaced by  $(4/\pi)(1-p_0)$ .

The question is most conveniently stated for the middle plane, x = a/2, inasmuch as the saturation here is least. If at 20°,



k = .23 cm<sup>2</sup>/sec, about, the graphs, Fig. 2, contain the relative saturation pressures, p, as ordinates, at the times given by the abscissas in minutes, according as the initial pressure is

$$p_0 = 0, p_0 = \frac{1}{3}, \text{ or } p_0 = \frac{2}{3}.$$

They imply successively greater saturation throughout. As the relative saturation left after any exhaustion would not probably be less than  $\frac{2}{3}$  even in the absence of convection, the inferior limit of saturation shown by these data is excessive.

Thus, in 3 or 4 minutes the air-plate in the trough may be considered saturated under the most unfavorable conditions. In the aspiration of fresh air through the trough the maximum rate was about 4.5 lit/min, the usual rate 1.5 lit/min. The capacity of the trough, including parts above the cloth lining, about 11.3 liters.

Hence 3 to 5 minutes suffice to renew the air and each particle remains in the trough from 1.5 to 4 minutes. The time needed for adjustments after the influx pipe is shut off and prior to sudden exhaustion was about 1.25 minutes. Therefore the total time for saturation was 2.7 to 5 minutes, which should suffice even in case of diffusion alone.

The conditions, however, are much more favorable as the influx and efflux currents evoke considerable convection. The lightness of water vapor is itself favorable to the same end. It is observed, for instance, on exhausting *immediately* after the introduction of phosphorus nuclei, that filamentary condensation is in evidence, denoting currents upward axially and downward near the walls of the receiver.<sup>1</sup> These fog strands are the inevitable convection currents due to the lightness of the vapor.

4. *Miscellaneous Tests.*—If there had been undersaturation the coronas found on condensation should have been larger in less saturated, and smaller in more saturated parts, which was not observed. Sudden exhaustion immediately after shutting off the influx showed a somewhat enlarged uniform corona, but even enlargement was not invariable.

The nucleation obtained with the fast or the slow influx specified was without marked discrepancy for reasonable differences of time; *i. e.*, such as would not involve time losses of nuclei. Cf. § 6.

The effect of a long influx pipe (10 meters of  $\frac{1}{4}$ -inch lead pipe) and of a short pipe 1 meter long could not be sharply differentiated, owing in a measure to the cotemporaneous variations of atmospheric nucleation. So the presence or absence of the coil in the water-bath (24 turns each about 3.5 cm. in diameter) was of small significance.

Experiments were made with regard to the usefulness of this coil in keeping the influx air at room temperature, both by filling the bath with abnormally hot water ( $40^{\circ}$  C.) and with broken ice. The effect on the apertures of the coronas was in both cases unimportant. Hence except on very cold days, the water-bath and coil may be withdrawn. The atmospheric air after traversing the 10 meters of influx pipe is already sufficiently heated to be introduced into the condensation chamber directly.

<sup>1</sup> Smithsonian Contributions No. 1373, 1903.

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Tests were also made with a U-tube loosely filled with wet sponges and with a half-filled drying tube one meter long containing phosphorus pentoxide. In neither case was a definite effect on the coronas ascertained.

Freedom from leakage was finally tested by filtering the air. The coronas on sudden exhaustion showed a gradual decrease to complete evanescence.

5. Diffusion from a Single Surface. — The case is naturally less favorable if the upper wet surface (double cotton cloth) is omitted. The computation may be made from an expansion of Kramp's integral so that

$$p = 1 - \frac{2}{\pi} \left( \frac{x}{(4kt)^{\frac{1}{2}}} - \frac{x^{3}}{3 \times 1} + \frac{x^{5}}{(4kt)^{\frac{3}{2}}} - \cdots \right)$$

where p is the vapor pressure relative to saturation at a distance x above the surface of the liquid at the time t for the diffusion coefficient, k = .23. The curves are given in Fig. 3 for x = 5 cm. the middle plane, and x = 10 cm. the top plane of the trough. When the initial saturation is 1/3 or 2/3, the coefficient  $2/\pi$  is to be modified as stated above.

If it were not for convection, therefore, such an apparatus would be unsuitable, for even after waiting five minutes, the air at the top, x = 10 cm., for an initial saturation of 2/3 is but .8 saturated from diffusion alone. At x = 5 where the observations are made, the saturation is nearly .9.

One might therefore expect to obtain distorted coronas campanulate in outline, small below and large above, whenever condensation is produced within a few minutes after closing the inlet. Yet such is never the case if less than a minute is allowed after influx ceases. Granting that two to four minutes are needed on the average for a particle to pass through the trough, as stated above, if exhaustion is made immediately after closing the top layer is but two thirds saturated. Under these conditions there is in fact an unusually large

of the influx pipe, the air may be regarded saturated except in the coldest weather.

6. Absorption and Decay of Nuclei.— The losses in the influx pipe are difficult to determine because of the variation of atmospheric nucleation. The observer is left in doubt whether a given difference is due to absorption in the pipe or to causes without.

The possibility of loss of nuclei on contact of dry air with the saturated gas in the condensation chamber is an independent question. It is also to be borne in mind that nuclei may possibly be produced by the sudden contact within the chamber. No evidence is forthcoming.

If the nuclei after being introduced into the receiver are solutions, some estimate of their persistence may be formed from my experiments on solutional nuclei, by treating the loss as if it occurred at the boundary of the vessel only. If the nucleation falls off from  $n_0$  to n in the time t and k is the absorption coefficient,

$$n/n_0 = \varepsilon^{-2(1/r+1/l)kt},$$

where r and l denote the radius and length of the cylinder in which absorption takes place. In case of comminuted pure water, k = 5to 10 cm./min., and the nuclei should quite vanish in a few minutes. Thus if

$t = I \min.,$	$n/n_0 = .154$
2	.023
3	.003

If the nuclei are derived from very dilute solutions like river water an average value, k = .1 may be taken, whence if

$t = I \min_{i}$	$n/n_0 = .96$
3	.89
5	.83
10	.68
50	.15
100	.02

phorus and other nuclei. Hence if the type of corona changes after one or two minutes' waiting, it may be considered certain evidence that the air is not saturated and the diffusion error predominating. Owing to the difficulty of avoiding either insufficient saturation or excessive time losses my later observations contain data for two different aspirating currents, the faster corresponding to about three minutes' sojourn of the nuclei in the receiver, the other to a time longer than five minutes. In this way the effects of undersaturation which are most to be feared are guarded against, while the faster current gives data falling short of the absolute nucleation by not more than ten per cent.

7. Effect of Pressure Difference. — It is next to be considered whether the pressure difference,  $\partial p$ , used in the exhaustions is pronounced enough to catch all the nuclei. This is of particular interest in view of the presumably low order of nucleations obtained.

The usual value,  $\delta p = 17$  cm. corresponds to the following pressure ratios and adiabatic temperature reductions in air  $[(76 - p')/(76 - p' - \delta p)]^{.41} 273 = \delta'$  if p' is the vapor pressure of water and  $\delta'$  the reduced absolute temperature.

10°.	Pressure ratio, 1.292	ઝ′ <del>=</del> 254.7
20	1.297	263.4
30	1.341	268.8

For comparison data were gathered with a larger pressure difference  $\delta p = 22$  cm., for which the values are :

<b>10</b> °	1.414	245.5
20	1.416	254.1
30	1.432	261.5

Clearly the coronas for the larger temperatures and temperature differences must be smaller, *cæteris paribus*, in view of the greater quantity of moisture precipitated. The data for m, the quantity of moisture precipitated per cubic centimeter of saturated air have been computed by the method of C. T. R. Wilson and J. J. Thomson<sup>1</sup> and are given in the following table :

<sup>1</sup>Cf. Thomson, Phil. Mag. (5), XLVI., p. 538, 1898.

Initial Tempera- ture. Vapor Density		Pressure Difference $\delta p = 17$ cm.		Pressure Difference $\delta p = 22$ cm			
	Vapor	Temperature Falls to			Temperature Falls to		
	Density.	For Dry Air.	For Wet Air.	<i>m×</i> 10 <sup>8</sup>	For Dry Air.	For Wet Air.	<i>m</i> ×10 <sup>6</sup>
°C.	×10 <sup>6</sup>	°C.	°C.		°С.	°C.	
10°	9.3	-18.3	- 4.5	3.7	-27.5	-10.1	4.2
20	17.2	- 9.6	+ 8.8	4.6	-18.9	+ 4.6	5.5
30	30.1	- 4.2	19.6	5.7	11.5	+17.0	6.7

Table Showing Grams of Water Precipitated per cu. cm., m.

Since  $m = n\pi d^3/6$ , if there are *n* fog particles per cubic centimeter each of the diameter *d*, and since sd = a where *s* is the aperture of the coronas with an arbitrary goniometer and *a* the corresponding constant,

$$s \sqrt[3]{m} = .806a \sqrt[3]{n},$$

which is constant for a given nucleation. Thus the relation between s' and s at  $\delta p = 22$  cm. and 17 cm., respectively, may be written

$$s'/s = (m/m')^{\frac{1}{2}} = .952,$$

In Fig. 4 the line s'/s has been constructed and the observations grouped with reference to it. The cases are usually too low; or in other words at the higher pressure difference,  $\delta p = 22$ , which requires a longer period of waiting after influx ceases, relatively *fewer* nuclei are entrapped. From this one concludes not only that from the medium if saturated all the nuclei are precipitated at  $\delta p = 17$ cm., but that at the higher pressure difference the time needed for adjustment is excessive and that the time loss of nuclei in the receiver frequently becomes appreciable.

8. Precipitation per Cubic Centimeter. — To determine *m* I originally proceeded as follows: In a mixture of *x* grams of vapor, *y* grams of air and I - (x + y) grams of water, the absorption of heat due to a rise of temperature  $d\vartheta$  at constant volume was taken as  $C[I - (x + y)] + hx + rdx/d\vartheta + cy$ , per degree, where *C*, *c*, and *h* are the specific heats of water, air at constant volume, and saturated vapor, respectively, and *r* the latent heat. Since  $h - C = dr/d\vartheta - r/\vartheta$ , *h* may be eliminated. Again the absorption of heat due to a volume increase

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absorption is nil and the equation thus obtained may be reduced eventually to

$$\frac{d}{d\vartheta} \{ rx/\vartheta + [C(1-y) + cy] lg\vartheta \} d\vartheta + yc(\gamma - 1) dlgv = 0.$$

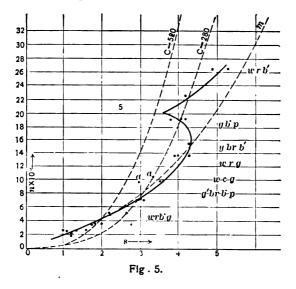
As this is not a perfect differential I assumed that the relation of v and  $\vartheta$  to be approximately that of air,  $v^{\gamma-1}\vartheta = \text{const.}$ , supposing that I could *subsequently* correct for the precipitated water by successive approximation. In this way one obtains at the beginning and the end of the exhaustion for any two temperatures  $\vartheta$  and  $\vartheta'$ , using accents throughout for the latter case, after integrating,  $x'/x = (\vartheta'/r')(r/\vartheta - lg\vartheta'/\vartheta)$ , where (x - x')/x is the mass ratio of precipitated liquid to the original vapor. In my work thus far the results were computed in this way and for  $\vartheta p = 17$  cm. were at  $10^{\circ}$ ,  $20^{\circ}$ ,  $30^{\circ}$ ,  $m \times 10^{6} = .59$ , 1.13, 1.85 grams respectively, where the corrections for precipitated moisture have been applied and  $\vartheta p$  is an isothermal value. If  $\vartheta p$ , the observed pressure reduction, were treated adiabatically the corresponding values of  $m \times 10^{6}$  would be .42, .76, 1.28.

The results for *m* so obtained will have to be rejected as they are much too small (probably because the pressure coefficients were overlooked) when compared with the results of experiments due to Schlagintweit and to Konrad. The latter found that a fog which limits visibility to about thirty paces contains about four grams of water per cubic meter, whence on the average  $m = 4 \times 10^{-6}$ , for instance. In the direct approximation of Wilson and Thomson (*l. c.*), the value of *m* is computed as an intersection, by making the *m* values compatible with the vapor density curve for water. The data calculated in this way have already been tabulated for the pressure difference  $\partial p = 17$ , in § 7, and they will be used in the following summary.

9. Relation of Nucleation and Aperture. — In the earlier work the nucleation n, was found directly from the apertures. s. of the coro-

Measurements of s would naturally be made as far as the inside of the red ring or the circumference of the (eventually) white disc: but in such a case they bring out very strong periodicity in the first place, and are soon subject to large errors due to the increasingly vague and washed outline of the disc. Hence measurement is more appropriately made to the dark blue ring which limits the green coronas or to the dark interior of the green ring in the crimson coronas. These lines are not only sharper but they reduce the periodicity. It is understood that with air nuclei and  $\delta p > 17$  cm., the green corona is seldom exceeded. Otherwise it would be necessary to increase the uniform pressure difference against which there is no objection other than the increased practical inconvenience.

If the old data for m be replaced by the new (§§ 7, 8), and if measurement of the aperture s be made as far as the *outer* edge of



the red ring, and if the results of special optical measurements sd = a = .0026 be inserted,  $n = 520 s^3$  at  $20^\circ$ , since  $m = 4.6/10^6$ . This equation, however, can have no application beyond the small normal coronas since for larger aperture s varies periodically with the number of particles or their diameters (Fig. 5).

Independent experiments were now made, and standardized by assuming arbitrary values of n for the two successive green coronas obtained with air nuclei and computing the effect of successive exhaustion, geometrically.

The graph for these results, Fig. 5, shows the marked periodicity culminating in the green corona. Without doubt the corresponding crest should again appear in the lower greenish coronas <sup>1</sup> as in fact the two observations marked *a* seem to require; but the coronas are now so closely crowded together that the true contours of the graph are extremely difficult to obtain. Moreover the least imperfection of the filter in case of small *s* and *n*, adds particles whose number can no longer be regarded as negligible, while the occurrence of subsidence becomes increasingly more important and below s = 1 cm. wipes out the coronas at once.

Conclusion. — In the above paragraphs I have endeavored to present the complications to which the method of coronal registry of atmospheric nucleation is incident, complications which were not anticipated and for which I was altogether unprepared. In the course of my work I made an unfortunate error in endeavoring to reduce the data to absolute values; but, apart from this, the greater number of discrepancies (as for instance the periodic distribution of nucleation in terms of aperture) could not have been foreseen at the outset. Nevertheless, the practical convenience of the method makes it well worth while to attempt further development, and I hope therefore soon to carry out a complete revision<sup>3</sup> of coronas in relation to nucleation, embodying all the details I have since learned.

In addition to the remarks made in § I, it seems to me that the variety and importance of the phenomena which are now attributed to the invasion of solar and cosmical dust into the atmosphere (such as certain variations of atmospheric pressure, of atmospheric electricity, of terrestrial magnetism, of auroral display, etc.), induce one to wonder why a continuous and systematic survey of atmospheric nucleation has not long since been included among the permanent records of observatories. Surely in discharging its re-

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#### DO FALLING BODIES MOVE SOUTH?

#### BY EDWIN H. HALL.

PART II.<sup>1</sup> METHODS AND RESULTS OF THE AUTHOR'S WORK.

THE exact place of my experiments was the axis of the inclosed, isolated tower of the Jefferson Physical Laboratory of Harvard University. The distance of fall available in this tower is very small compared with the vertical distances which most of my predecessors in this research have used; but some compensation for this disadvantage is found in the fact that the tower is very well protected from disturbances due to winds or lateral inequalities of temperature, and in the further fact that in working within a laboratory I could have at hand all needed appliances and assistance.

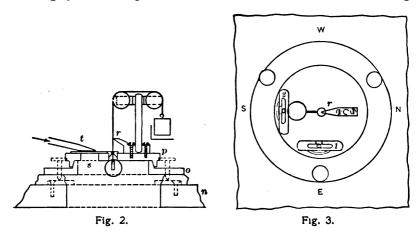
The general plan and arrangement of apparatus is indicated by Fig. 1. At the top a wooden box a, having a trap door on one side and a window on the other, carries on its upper surface a contrivance of brass, in contact with which the ball to be released, a sphere of bell-metal 2.54 cm. in diameter, is held (see Fig. 2). The box  $\alpha$  is supported by means of two strong joists, not shown, the ends of which rest upon and are fastened to a railing, which crowns the tower. Beneath a, and separated from it by a layer of cotton, is a square of board, b, having a central circular hole about 34 cm. in diameter, from the circumference of which is suspended a tube, c, of seam-Flg. 1. less cotton cloth ("pillowcasing") of the same diameter as the hole. The board b, is supported from the roof over the tower, and therefore has no rigid connection with a save by way of the base of the tower. The cloth tube, distended by five circular ribs of stout wire, extends downward about 20 m. to d, a rectangular opening, about 30 cm. by 40 cm., in the vaulted ceiling of the con-

<sup>1</sup> A third paper on Preliminary Experiments, Variations of Method, etc., in the author's work will be published in the Proceedings of the American Academy.

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stant temperature room, which is the lowest story of the tower. The lower end of c is attached to a square of board similar to that at the top. On this lower board are placed weights aggregating about 8 kgm. to keep the tube taut, and outside it, separated from it by a narrow space stuffed with fibrous material, is a casing of wood, e, to prevent lateral movement. Below d is shown, unsupported in the figure, a pan, f, filled with some mixture of tallow and beeswax, into which the ball is to drop. The board, g, now shown beneath the ball at the top of a, is a guard so placed as to arrest the ball if it is dropped prematurely, but free to swing around out of the way when the road is to be cleared.

Fig. 2, the scale of which is 1 to 4, shows in vertical section, and Fig. 3 shown in plan on the same scale, details of the releasing



apparatus. In this figure n is the wooden top of the box a of Fig. I. Screwed to n are three (two shown) brass disks, No. I having in its top a conical pit, No. 2 having a V-shaped groove extending toward No. I, No. 3 being plane, which are the bases of the leveling screws supporting the brass plate o. The slight looseness of fit of these screws in the holes bored through the plate is very nearly abolished by the action of strips of spring brass attached to the under side of the plate. The arrangements thus indicated make this plate very firm in its place, while leaving it all desirable freedom of adjustment. On o rests the brass plate p, the two meeting in a conical bearing at which o furnishes the internal

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and p the external part. To the upper surface of p is screwed a brass block having a beak r, against the tip of which rests the fine thread (or wire) which bears the weight of the ball before its release. Inclining slightly from the vertical at r this thread passes over pulleys to a counterpoise, which was usually a weight about 20 gm. heavier than the ball. The thread holds the ball close against the very slightly beveled lower end of a hole, 0.9 cm. in diameter, in the center of the plate p. The upper part of this hole is partly filled by a plug having a central hole 0.2 cm. in diameter through which the thread extends. The object of this plug is to prevent disturbance to the starting ball from the small gas flame, which, emitted in a puff from the tube t, is used to burn off the thread.

The lower end of the thread passes through a very fine hole in the top of a brass plug,<sup>1</sup> about 0.4 cm. wide and 0.5 cm. long, which is screwed into a hole bored about 1.4 cm. deep into the This plug was drilled nearly through from the bottom, and ball. the thin cap thus left at its top was punched through with a fine needle to admit the end of the thread, which after passing is knotted below so that it cannot be withdrawn. The object of making so deep a hole in the ball is to lower its center of gravity and so diminish the possibility of its rotation about a horizontal axis during fall. The method of placing the ball after the attachment of the thread was as follows: The gas tube t, and the thin brass plate lying just beneath it over the hole s, having been removed, the plug shown above the ball was lifted out of place and the free end of the thread passed through it and attached to the counterpoise; the ball was then lowered through the hole s, and brought to its place beneath the central hole, the thread passing along through a narrow slit, see Fig. 3, connecting the two holes; the plug was dropped into place, the thread adjusted in a certain file mark in the projecting beak r, and led carefully over the pulleys. As the thread was very slender, so as to be cut off instantaneously by the merest whiff of flame, the operation just described was attended by considerable

<sup>1</sup> Previous to May 28 a hard-rubber plug having a loop of thread projecting from the center of its top was used here, the upper thread being tied into this loop. Apparently the change of plug made no difference in the behavior of the balls, but the brass plug has a neater look.

risk of a premature and misguided fall of the ball, which, if not arrested by the guard shown in Fig. 1, might have done serious damage to the assistant or the apparatus below. Before release of the ball, the hole s and the slit leading from it were covered, as in Fig. 2, to lessen air currents. For the same purpose the space between the board n and the plate o was stuffed with cotton.

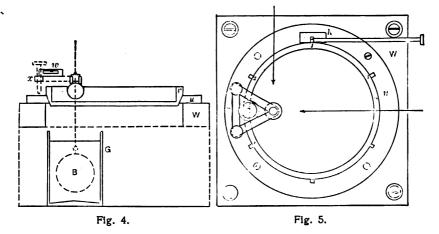
Fig. 3 shows, with some omissions, the transmitting apparatus as seen from above. The letters N, E, S and W, here mark approximately the points of the compass. The experimenter was always on the east side. In this figure 1 and 2 are the spirit-levels used in adjusting the plate from which the ball was to be dropped. As a rule, this plate was carefully leveled shortly before the dropping of each ball. On the side of each level is a curved projection, which I have called a loop, and each is here shown with its loop on the outer side, a condition designated as "loops out." Turning each level end for end we get a condition which is called "loops in." Substantially half the levelings were made with "loops out" and half with "loops in," the endeavor being in both cases to bring the ends of each bubble opposite two marks made on paper fastened alongside. The "beak" r is here shown pointing south, but by rotating the plate on which it rests the beak can be made to point north. Half the balls were dropped from "beak south" and half from "beak north," the change of position being made, usually, at the middle of each "pan" of six balls. The conical bearing of the upper plate p, Fig. 2, against the lower plate o, though very good, the two having been ground together, was not perfect, so that a slight rocking of the upper plate could occur, and after each turning of the upper plate through 180° a perceptible readjustment of the level was usually made. There was, apparently, no lateral relative movement of the two plates except through this rocking. With "beak north," level No. 2 was on the north side of the apparatus; but level No. I remained on the east side with both positions of the beak. The possibilities of error from faults of leveling have been carefully considered, but will not be discussed here.

Thus far, the only use mentioned for the beak r is to control the course of the thread which carries the ball; but in a different phase

of the work it fixed the position of the plumb-line, an even more important function, for the position of the ball just before release was determined almost wholly by the position of the central hole of the plate p, whereas the position of the plumb-line was determined entirely by the beak. As the object of the whole research was to find how far the center of the ball deviated from a vertical line during its descent, it was of prime importance that the mean position of the plumb-line, which mean was the vertical line used in the comparison, should pass as nearly as might be through the mean position of the center of the ball before release. The upper part of the plumb-line was usually a silk thread, though previous to May 23 it was sometimes a fine copper wire continuous with the main part of the suspension, and this thread or wire rested across the beak in the same file mark which at the proper time held the thread carrying the metal ball. Care was taken, with the help of devices not shown in the figures here given, to place this file mark very nearly over the center of the hole which fixed the position of the ball; but it was hardly possible to make this adjustment perfect, and even if it had been so the thickness of the suspending threads would have remained for consideration. Accordingly, the practice, already mentioned, of rotating the plate p, so as to make half the levelings and settings with "beak south" and half with "beak north," was adopted, with the reasonable hope of thus eliminating any appreciable error due to eccentricity of the beak. The change of position of the plumb-line caused by rotating the plate through 180° was, after releveling, much of the time less than one 0.02 cm, and sometimes less than 0.01 cm.

A few centimeters below the releasing plate the plumb-line became a bare copper wire 0.016 cm. in diameter, which previous to May 23 reached down to the bob, an ivory sphere (B, Fig. 4), nearly 6 cm. in diameter, immersed in water to check vibrations. On and after the date just mentioned a short piece of No. 38 copper wire, about 0.010 cm. in diameter, was used for the lowest part of the suspension, the coarser wire being rather too thick for satisfactory observation through the two very short range telescopes (see Fig. 7) used in reading its position. At first a smaller vessel than the jar G in Fig. 4 was used for holding the water surrounding the plumb-bob; and in it the ball came to rest very promptly and remained very steady; but the danger of contact between the ball and the side of this small vessel led me to use finally the larger vessel here shown. Working alone in the room at the bottom of the tower, with the door closed, and avoiding hasty movements of my body, I had little trouble from vibrations of the plumb-line, and could make satisfactory observations of its position; but when inexperienced spectators were present in this room, I was obliged to defer this part of my work.

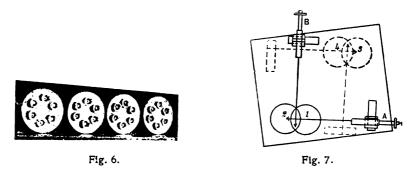
Figs. 4 and 5 show in some detail different aspects of the receiving apparatus. W is the wooden top of a low bench, which



rests upon and is screwed fast to the top of a strong table, not here shown, which will be considered in connection with Fig. 7. Resting on W, and screwed fast to it, is a brass ring u, which supports, in a ground conical bearing, the brass pan v, which contains the mixture of tallow, etc., into which the ball falls.<sup>1</sup> Projecting from the side of the pan, Fig. 5, are brass studs, 1, 2, 3, 4, 5 and 6, by means of which, caught by the clamp k, the pan is secured in any one of six positions, in each of which it catches a ball. See Fig. 6, which is made from a photograph showing the balls dropped

#### No. 4.] DO FALLING BODIES MOVE SOUTH? 251

in one evening. To locate the vertical passing through the center of a ball after its lodgment in the tallow, a device indicated on the left in Figs. 4 and 5 was used, x being a tripod, two corners of which are supported by leveling screws resting on the brass ring u, while the third, through which is a vertical hole 0.9 cm. in diameter, is seated carefully on the firmly imbedded ball. Fitting accurately in the top of this hole is a brass plug ending above in a sharp point. On this point, after the tripod had been adjusted by the help of a small spirit level (w, Fig. 4), observations were made by means of the same telescopes which had been used to find the position of the plumb-line. Readings of the micrometer screws of



these telescopes were made and recorded to the nearest one hundredth of a turn, which corresponded nearly, in one case, to 0.002 cm., and, in the other case, to 0.001 cm., in the position of the vertical to be determined.

Each of the telescopes was carried by a stiff wooden support consisting of a V-shaped trough screwed to a block, which in turn was screwed to the table top (see Fig. 7). A is shown looking west<sup>1</sup> and B looking south, their lines of sight crossing at a point which indicates the position of the plumb-line. Circle I indicates

<sup>1</sup> The edges of the table in this figure correspond nearly to the points of the *compass*, while the lines of sight of the telescope are meant to be true east and west and north and south, respectively. The angle between the two sets of lines was at first laid out by

the first position in which the receiving pan was placed, April 26 to May 28; circle 2, the second position of the pan, May 31 to June 17; circle 3, the third position, reached by turning<sup>1</sup> the table, and all which it carried, 180°, June 21 to July 8; circle 4, the fourth and last position, July 9 to July 25. The significance of these four positions requires, perhaps, some explanation. With the pan in position 1, for example, the ball falls much nearer to the western than to the eastern side, and this condition may affect somewhat the easterly deviation; for, on the one hand, the tallow is somewhat harder near the edge than near the middle, a circumstance which tends to push the ball toward the middle, while, on the other hand, the tallow sometimes crumbles and breaks away more on the side toward the near edge than on the other side, a circumstance which deflects the ball outward from the middle. Of these two opposing influences it is probable that the one acting toward the center is the more effective, on the average; but, as it was impossible to tell just how great the resulting error might be, it was necessary to make two series of experiments, one with the pan in position I, the balls falling in its western side, the other with the pan in position 2, the balls falling in its eastern side. Later I turned the table through 180°, thus bringing the pan to its northeast corner, and made two more series of experiments, one with position 3, the other with position 4.

All of the balls of which account is here taken were dropped at night, work usually beginning between 7 and 8 o'clock and lasting about three and a half hours. Previous to May 26 the work at the top of the tower was usually done wholly by myself, the work at the bottom being done by an assistant, the routine being as follows: Leveling of top plate, with plumb-line hanging from beak (pointing south), readings of the position of the plumb-line by means of the telescopes at the bottom, reversal of the top plate to "beak north" position and releveling, readings on plumb-line after this reversal, removal of plumb-line, placing of ball at the top (Fig. 2) and pan at the bottom (Fig. 4), release of ball, measurement of position of ball in pan, etc. After all the balls for the night's use

<sup>&</sup>lt;sup>1</sup> The crossing point of the arrows in Figs. 3 and 4 was made coincident with the crossing point of the arrows in Figs. 1 and 2 by moving the table toward the southwest.

had been dropped, the plumb-line was replaced on the beak, and observations similar to those at the beginning were made upon it.

On and after May 26 the routine was somewhat different : Leveling and reversing the top plate, with plumb-line on beak, by an assistant, readings of position of plumb-line by myself at the bottom, removal of plumb-line, leveling of plate and adjustment of ball by myself at the top, adjustment of pan at the bottom by the assistant, release of ball by myself, readjustment of pan by the assistant, etc. After three balls had been dropped into any pan, the release plate was reversed from "beak north" to "beak south" or vice versa, and the next three balls were dropped into it from the plate in its new position. After all the balls, usually twenty-four a night, had been dropped, the plumb-line was replaced on the beak, the assistant and I changed places once more, and observations on the plumbline were made again. After this each pan in turn was put back into place, and observations were made by myself on the position of each ball, my assistant adjusting and leveling the tripod (Figs. 4 and 5).

Each pan of six balls was treated as a unit in calculations. That is, no fraction of a pan was counted. If any accident occurred which required the rejection of any one ball in a pan, the whole pan was rejected. The only accidents which were held to justify such rejection were those cases in which, before the use of the guard g, Fig. 1, a ball had been dropped unintentionally or had struck an obstacle in its fall, or had found the tallow too soft.<sup>1</sup> Mere divergence of a ball from the ordinary path, provided it had been dropped under apparently usual conditions, was not regarded as sufficient reason for excluding this ball, however great its divergence might be. There was no "criterion for the rejection of doubtful observations" based on the magnitude of supposed errors. The method followed was to bury exceptional cases beneath the weight of num-The extreme range north and south and east and west per bers. pan was, on the average, about 0.5 cm., the improvement in this respect from April 26 to July 25 being very small, in spite of conThe results obtained, after much preliminary work ending April 23, are as follows :

Date, 1902.	Position	Mean Deflection.		Probable Error.		No.
	of Pan.	s	E	Of S	Of E	of Balls,
April 26 to May 28	1 (Fig. 7)	0.0057 cm.	0.163 cm.	0.0083 cm.	0.0093 cm.	258
May 31 to June 17	2 "	-0.0038 ''	0.149 "	0.0103 "	0.0093 "	210
June 21 to July 8	3 "	-0.0011 "	0.189 "	0.0070 "	0.0091 "	240
July 9 to July 25	4 "	0.0249 ''	0.082 ''	0.0101 "	0.0103 "	240
General means,		0.0050 cm.	0.149 cm.		Total	-= 948
Probable error, 1	st	0.0043 ''	0.0047 "			
** ** 2	d	0.0039 "	0.0146 "	•		

In taking the "general mean" each S or E was given a weight inversely proportional to the square of its probable error. The probable error marked "Ist" of the general mean was reckoned from the four individual probable errors, on the assumption that the main differences between the deviations, for the four positions of the receiving apparatus, were not the result of casual errors, but were due to certain fixed conditions which the combination of the four positions would eliminate from the result. The probable error marked "2d" was reckoned on the assumption that each of the four positions should have given the same result. This latter assumption is, for reasons already shown, far from correct in the case of the easterly deviation, and accordingly it gives a large probable error for that case.

Cajori gives as the formula of Gauss for the easterly deviation, without air resistance,

 $E_1 D_1 = \frac{1}{8} \cos \varphi g u t^3.$ 

where  $\Phi$  is the latitude, g the acceleration of gravity, u the angular velocity of the earth on its axis, and t the time of fall. With this formula I get as the easterly deviation which should have been found in my experiments, if they had been carried out with perfect accuracy in a vacuum, 0.179 cm. The mean easterly deviation actually found in these experiments, 0.149 cm., differs 0.03 cm. from this theoretical value, a quantity too large to be accounted for by the resistance of the air. I attach but little significance to this discrepancy, as the conditions for determining the easterly deviation in my work were plainly not so good as those for determining the southerly deviation.

## NICKEL NITRATE.

## THE THERMO-ELECTRIC BEHAVIOR OF NICKEL NITRATE.

#### BY WM. MCCLELLAN.

#### HISTORY.

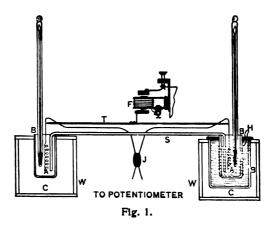
N 1825 Walker<sup>1</sup> showed that when a hot and cold platinum wire are plunged in an electrolyte a current of definite directions results. In 1832 Faraday<sup>2</sup> repeated this experiment by putting two wires in the electrolyte and heating the portion around one and cooling the portion around the other. Gore,<sup>3</sup> in 1884, working with a number of electrolytes, showed that the potential difference depended upon the concentration of the solution. Bouty,<sup>4</sup> working with a number of electrolytes and different electrodes, found the thermo-electric power to be independent of the concentration. In 1887 Ebeling<sup>5</sup> did some very exhaustive work with copper and zinc electrodes in salts of these metals and found that the potential difference did depend upon the concentration. He also found that the maxima for salts of the same acid happen at the same temperature point and also that their maximum points correspond with the maxima of conductivity. Hagenbach,<sup>6</sup> in 1894, did the most recent and the best work in this line. He gives curves for a number of sulphates and chlorides with platinum and other electrodes which show considerable regularity. He states, however, his inability to get any satisfactory results with electrolytes containing nickel or Bouty<sup>7</sup> tried nickel sulphate with nickel electrodes and nitrates. found that an external current flowed from the cold electrode to the Hagenbach repeated this experiment and found that no warm. definite values were obtainable, the action being very erratic, some-

> <sup>1</sup> Walker, Pogg. Ann., 4, p. 327, 1825. <sup>2</sup> Faraday, Researches, Soc. 17, p. 1932, 1840.

times positive and sometimes negative. With nitrates he could get nothing. Silver and cobalt salts are probably negative, but very inconstant. In view of these facts it was thought advisable to investigate the nitrates, particularly nickel nitrate, and see if any more definite results could be obtained.

#### ARRANGEMENT OF APPARATUS.

Fig. 1 shows this quite clearly. The solution was contained in the small beakers (B) and about 5 cm. deep and 3 cm. in diameter connected by a tube (S) of 15 mm. bore. The electrodes (A) were of platinum wire fastened to the ends of a light strip of wood (T), and continued out to (J). Here they were connected to copper wires which went to the potentiometer at J. The junctions were wrapped in thin silk and then wrapped close together in order that both junctions might be always at the same temperature. The



light stick (T) was fastened to one of the bars of an electrically driven tuning fork (F) which made about 256 V. S. The beaker (B) at the cool end was hung in a wood box (W) and packed around with raw cotton. The beaker at the warm end was hung in a larger beaker (Bl) containing water and a heating coil (H). A current of 3 amperes in this coil would raise the temperature of the water from 20 to 80 degrees C. in one hour. The theromometers were ordinary mercury in glass the mometers calibrated for the work. Measurements of E.M.F. were made by means of a No. 4.]

Leeds Potentiometer. The latter was calibrated by means of a Weston Cadmium Standard Cell, with practically zero temperature correction. By moving a single switch on the instrument the contacts could be changed from the thermo-element to the standard cell. It was thus very convenient to test the calibration of the instrument after each observation of the thermo-element. The instrument was of the latest type and had means of reading to 0.000001 volt. The D'Arsonval Galvanometer used permitted readings to this accuracy, though usually it was purposely not done owing to the rapid changes in potential difference.

#### SOLUTIONS AND ELECTRODES.

The solutions were all made with Kahlbach chemicals in pure distilled water free from ammonia. The nickel nitrate solution had 14.530 g. of crystalline salt to 500 c.c. of water. The solution was mixed cold and used in this way for the earlier curves. The solution was boiled for some later curves, and the concentration corrected by the addition of boiled water. As suggested by Hagenbach, the platinum electrodes were rinsed first in boiling water, then in nitric acid, then in water, then in alcohol, and finally heated to incandescence. This whole treatment is necessary after the electrodes have been used for even one curve. The writer tried omitting each part in turn, and found that it was not permissible. One must be particularly careful to make the nitric acid treatment complete. It is better to take one curve per day, leaving the electrodes in the nitric acid all the night before. If this is not convenient, boiling in nitric acid for about ten minutes is a good substitute. It seems more than likely that there is a slight deposit of nickel during the progress of the curve, and it is very necessary to dissolve this off entirely. The wire form of an electrode was used on account of its adaptability in In the earlier experiments it was thought desirable to have design. the electrode in the form of a small coil surrounding the thermometer bulb, so that the temperature of the electrode might be obtained as accurately as possible. When the vibrating method was attempted this was found impracticable, so the arrangement shown in Fig. 1 was adopted. The writer supposed that the size of the electrodes would have little to do with the resistance of the cell, *i. e.*, that the

resistance would depend chiefly upon the length and connection of the tube (S) (Fig. 1). Some preliminary experiments showed that this was not true. At one time, when the electrodes were straight wires, dipping about 5 mm. into the solution, a most uniform curve was obtained, but on testing the sensibility of the apparatus it was found to be enormously reduced. Were this not so, and it may not be so, for much larger electrodes, - say plates, then the same current would polarize the large plate much less and so eliminate the trouble to a greater extent. It may be well to say here that the writer has never worked with anything more sensitive than this cell. The greatest care had to be used in handling the potentiometer key. By holding the key down at the proper times the galvanometer could be deflected at will to show a positive or negative potential difference. Frequently when trying to adjust the potentiometer, the polarization seemed to keep just a little ahead of the adjusting, and it was necessary to make a big jump and so overreach it. This was particularly necessary when the electrodes had not been sufficiently treated with nitric acid. It was in trying to eliminate this trouble that the necessity for the complete acid treatment was observed.

Ebeling found,<sup>1</sup> as well as some others, that zero potential difference could not be obtained from two wires made in the same way and treated in the same fashion. Hagenbach<sup>2</sup> was unwilling to complete a curve unless this initial potential difference was less than 0.02 volt. The writer, in order to obviate this difficulty as much as possible, took a long piece of platinum wire and cut it at the middle. The resulting ends were then treated and used as electrodes. Towards the last it was found possible to set up the cell and have the initial potential difference as low as 0.005 volt regularly.

### DETAILS OF EXPERIMENT.

The electrodes and solution were first prepared as has been described. Then the solution was put into the two beakers. One end of the tube (S) was suddenly thrust into one of the beakers, while the other end was depressed, which caused the solution to start immediately through the tube. The open end was then put

> <sup>1</sup> Ebeling. See before. <sup>2</sup> Hagenbach. See before.

into the other beaker. The electrodes and the thermometers were then placed in position and the whole allowed to stand until the temperature became steady. This sometimes took several hours, but usually if conditions were properly arranged, it was unnecessary to wait more than an hour. Contrary to expectation, it seemed rather difficult to get both solutions to exactly the same temperature, though the respective temperatures remained very steady.

The initial potential difference was now read. If found to be high, the electrodes were removed and again treated as described, and replaced. If the initial potential difference was below 0.02 volt, the temperatures were read and the heating current turned on. At first the temperature was caused to rise from 20° to 80° C. but as soon as the erratic nature of the curves was seen, the change was made from 20° to 50° C., as it seemed a waste of time to use the larger interval when the smaller gave no regular results. Some preliminary curves were taken by sending an exceedingly small current through the heating coil, and then waiting for the temperature to become constant; then increasing the current by steps and waiting each time. This method has several disadvantages, it takes many hours to get a curve, with the concentration changing during the interval, and changing more rapidly at the warm end than at the cold. This is particularly marked at the higher temperatures, when the evaporation is rapid. It was found to be much better to cause a larger current to flow through the heating coil, and measure the potential difference at different points as the temperature rose slowly. Usually the current was fixed so that there was a rise of about 30° C. per hour. The details of the vibrating electrodes, etc., will be given in the description of the curves.

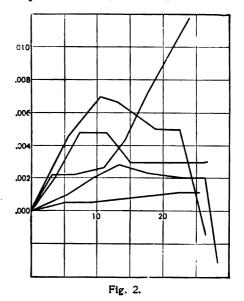
### THE CURVES.

## (a) Stationary Electrodes, Unboiled Solution.

The curves shown are those obtained, Fig. 2, with stationary electrodes in unboiled solution; Fig. 3 with vibrating electrodes in unboiled solution; Fig. 4 with stationary electrodes in boiled solution.

WM. M'CLELLAN.

The curves of Fig. 2 are very erratic. There was n in balancing the potentiometer, however, and the curv



Data for Fig. 2.

t = 23°	v = .002	t = 22.6°	v = .0098	t = 21°
V 1	T	v	T	V
.0000	0	.0000	0	.0000
.0005	5.1	.0022	2.8	.0045
.0005	9.6	.0022	6.8	.0070
.0008	16.0	.0027	11.0	.0065
.0011	22.7	.0042	14.2	.0005
.0011	25.4	.0072	17.5	.0005
		.0101	21.5	0014
		.0122	22.9	0014
t = 21.5°	v = .003	t = 22.5°	v = .005	
V	<i>T</i>	v	T	
.000	0	.0000	0	
.001	5.4	.0020	3.3	
.002	9.3·	.0042	7.1	
.0027	13.3	.0047	11.3	
.0023	17.7	.0047	15.2	
.000	23.2	.0030	20.1	

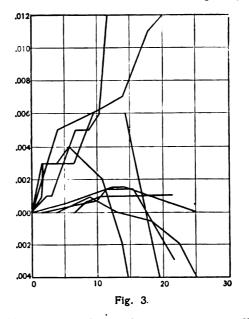
t = 25°	v = .003	t = 25.9°	800. — = v	t = 21.5°	t/ = .023
V	T	V	т	V I	T
.000	0	0	0	0	0
.003	1.6	.001	2.2	.001	1.5
.003	6.5	.001	3.1	.003	1.9
.006	9.6	.005	6.7	.003	3.9
.007	14.0	.005	8.7	.004	5.7
.011	17.9	.006	10.4	.002	10.8
.012	20.1	.029	11.4	002	13.8
.013	22.4			013	15.5
				015	18.3
				017	19.6
t = \$1.5°	v = .012	<i>t</i> = 19.5°	v =003	t = 23.8°	v = .003
V	T	V	T	V	T
.0000	. 0	.000	0	.000	0
.0000	2.3	.005	4.15	.000	3.9
.0000	4.3	.006	9.25	001	9.0
.0000	6.6	.006	14.25	.000	13.0
.0005	7.7	008	20.65	0005	18.0
.0010	10.3	0051	23.35	002	22.3
.0010	14.2			011	28.1
.0010	17.6				
.0010	19.2				
.0010	21.4				
t = 22.0 <sup>0</sup>	v = .005	t = 22.6°	v =001		
V	T	v	T		
.0000	0	.0000	0		
.0005	5.	.0000	2.0		
.0015	12.3	.0007	10.0		
.0015	14.0	.0014	11.5		
.0010	17.6	.0014	15.6		
.0000	24.9	0030	21.6		
		0110	26.1		

Data for Fig. 3.

they are, were easily obtained. In all the curves, the positive sign means that the current flows in the external circuit from cold to hot. In plotting these curves I have plotted rise of temperature (T) as abscissas and change in potential difference (V) in volts as ordinates. At the heads of the columns, v indicates the initial potential difference in volts, and t the temperature at the cool electrode. The curves of Fig. 2 are all positive. A large number of curves taken earlier in the work show a far greater variation, partly negative and partly positive. These are the best series that it was possible to obtain with stationary electrodes and unboiled solution. While taking a curve, the experiment of shaking the electrodes was tried just after balancing the potentiometer and the balance was greatly disturbed. This led to the experiment of vibrating electrodes.

## (b) Vibrating Electrodes, Unboiled Solution.

Vibrating electrodes have been used very much in electrolytic deposition recently and have been found very advantageous, both vibrating anodes and vibrating cathodes. The writer has been unable to find any data relative to the particular application here employed, that is, very rapid vibration with very small amplitude. The amplitude used here varied from 1 mm. to 3 or 4 mm. — never



greater than this. Fig. I shows the arrangement sufficiently well. It is very evident that an electrode vibrating under these circumstances would of necessity stir in a more or less amount of air and this would certainly affect the result. The curves of Fig. 3 indicate two general groups, one in which the curves show a rapid rise in potential difference, and the other in which the rise is comparatively slow. Three of the curves show a change of several degrees No. 4.]

before any effect is noticeable and then the rise is sudden. In all the curves of the latter group it was noticed that there was little or no disturbance where the electrode pierced the surface, that is, there was little air stirred in, whereas in the former group, the electrode had considerable amplitude at the surface. The motion of the electrode was chiefly horizontal. Frequently on setting up the apparatus, the potential difference was read before starting the vibration, and again afterwards. The effect was quite sharply marked, If there was a great difference in the two readings, an examination

t = 24.3°	v =015	t == 22.8°	v = .0095'	t = 21.90	v0000
_ <i>v</i>	T	V	T	v	T
0	0	0	0	.0000	0
0	1.9	0	4.8	.0000	2.4
.0004	6.1	0001	9.3	.0000	5.6
.0004	10.4	0001	11.2	.0001	9.4
.0006	15.3	0004	15.1	.0001	13.2
.0006	17.2	0005	18.8	.0001	16.6
.0009	21.1	0002	22.9	.00015	20.4
.0014	24.3	.0007	25.2	.00020	24.3
.0017	25.9	.0014	26.5	.00020	26.7
t = 22.7°	v =001	<i>t</i> = 22.1°	v = .006	t = 28.9°	v = .0000
V		V	T	<i>v</i>	T
.0000	0	.0000	0	.0000	0
.0000	6.9	.0002	4.5	.0007	6.1
.0000	9.9	.0002	8.5	.0020	11.3
.0009	14.2	.00035	13.9	.0012	15.5
.0037	18.9	.00050	20.5	.0005	18.2
	,	.00050	25.4	.0005	21.0
		.00050	28.6	.0005	22.8
				.0005	24.3
	:			.0005	25.3
t = 23.3°	v =007	<i>t</i> = 24.1°	v =003		
V		v	T		
.0000	0	.0000	0		
.0000	3.0	.0000	3.2		
0001	8.0	.0001	8.2		
.0001	12.0	.0001	12.2		
.0004	16.9	.0001	16.6		
.0004	20.9	.0005	18.5		
.0020	25.4	.0009	22.2		
	•	.0011	25.7		

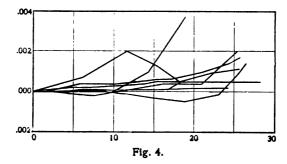
Data for Fig. 4.

of the electrodes showed considerable disturbance at the surface. When this was removed, the two readings were usually exactly alike, or else the reading with the vibration on settled down to a steady value though different from that with the vibration off. Many times when the balance with electrodes stationary was hard to obtain, the vibration was started and a reading taken easily, and on stopping the vibration the reading was found to be the same for some time, but would after a while become variable again. This was evidently due to the presence of free air in the solution, for no such trouble ever occurred with solution that had been boiled. When an unsteadiness in the potential difference was noticed in a boiled solution, it could be removed by again treating the electrode with nitric acid. Often no permanent balance could be obtained with the vibrator not working, but could be obtained when the vibrator was started. With too much motion at the surface, the difference in the two readings was sometimes 0.005 volt. No curves in any case were taken until the readings under same conditions were uniform for at least five minutes. Several times the cell was set up and readings of both kinds taken at intervals of an hour with little difference in the observations. It was absolutely necessary to keep the vibrating electrode from touching any part of the apparatus such as the thermometers or glass parts. When this occurred it was found impossible to balance the potentiometer.

#### (c) Stationary Electrodes, Boiled Solution.

These curves (Fig. 4) show a very marked improvement in regularity. Of the eight curves shown, two show a negative tendency, one of these, however, a very slight one, which soon becomes positive. All the curves show a very much smaller rise than had been found under other conditions. The solution was allowed to boil long enough to expel all air bubbles, and then put away to cool. Experiments were tried, by boiling the electrolyte in one of the beakers, and not pouring it at all, but simply allowing it to siphon over. This was tried several times, with the idea that probably the pouring from the vessel, in which the solution had been boiled, into No. 4.] NICKEL NITRATE.

could be observed, however, and the pouring evidently did little harm. It should be noticed that five of the eight curves show no change for at least three degrees' rise, and several of them for much more. Preliminary experiments with vibrating electrodes in boiled solution showed that the regularity would be much reduced by the vibration, probably on account of stirring air into the solution out



of which it had been boiled. No curves with this method were taken for this reason.

#### SUMMARY.

From the final curves shown it is reasonably certain that the thermo-electric power of the electrolyte used is nearly zero. The extreme sensitiveness of the cell to polarization explains of course, the real trouble in the measurements. This accounts for the presence of positive and negative curves when the greatest care is taken in the observations. It is absolutely necessary to have the electrodes in a definite condition at the start. This is not to have simply a low initial potential difference, but because a high initial potential difference means the presence of nickel on the electrode, and this means ease of polarization, and consequently, non-uniform No amount of heating to incandescence would remove results. this. A prolonged bath in strong nitric acid is the only effective process. Unless the electrodes have been treated thus, the potential difference is not constant at constant temperature. That is, the changes in national difference which take place due to the polariz-

tains air, the vibration has a steady effect, if the vibration does not stir more air into the solution. If any good result is to be obtained, the electrodes must be arranged with nodes at the surface of the electrolyte. A number of interesting effects might be obtained if a cell were designed in which the vibrations could take place without vibrating the surface, or if the part vibrating at the surface were insulated so that it did not form part of the electrode proper.

The presence of air in the solution causes great irregularity. Therefore boiling the solution free from air has a marked effect on the potential difference. Here the removal of the air shows the masking effect of the polarization much more easily. If the thermoelectric power amounts to anything it is probably positive, that is, it flows from cold to hot externally. In this connection it might be mentioned that the curves of sulphates and chlorides as shown by Hagenbach<sup>1</sup> show changes in potential difference of from 0.01 to 0.15 volt for a temperature rise of 60 degrees C., whereas an observation of Fig. 4 shows that in the case of nickel nitrate the rise would not be over 0.001 volt, even with polarization effects added on, or subtracted as the case may be. It is purposed to go on with this work until, if possible, an exact value is obtained for this effect whether zero or otherwise.

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<sup>1</sup> Hagenbach, see before.

# ON METHODS OF MEASURING RADIANT EFFICIENCIES.

BY E. L. NICHOLS AND W. W. COBLENTZ.

EVER since the publication of the paper of Julius Thomsen<sup>1</sup> on the Mechanical Equivalent of Light, in which he described the method of separating the luminous from the non-luminous energy of flames by the interposition of a water cell, it has been the general practice of students of artificial illumination to estimate radiant efficiency by some modification of his method.

It was the practice for many years to use instead of water a solution of alum, this substance being supposed to possess more complete opacity for the infra-red than water alone. Melloni is commonly cited as authority. Table II., however, on page 165 of the *Thermochrose*; in which the transmission of the rays of an Argand burner, by twenty-eight different liquids contained in glass cells is given, shows that according to his measurements such a cell containing a solution of alum transmitted 12 per cent. while the same cell when filled with distilled water allowed 11 per cent. only of the radiation to pass.

In 1893 Ernest Nichols,<sup>2</sup> who studied the transmission spectra of various substances in the infra-red, showed in a much more definite and conclusive manner the almost complete identity with water of the solution of both potassium alum and ammonium alum, as regards their transmitting power. Indeed in the case of solid alum it to the doubtless to the water of crystallization rather than to the salt that the opacity is to be ascribed.

That neither water nor alum in solution, which may be regarded as identical with the former as regards its transmitting power, fulfills even approximately the conditions necessary to a screen for the separation of the non-luminous radiation has long been known, and it has been customary to make a correction for the imperfect opac-

<sup>&</sup>lt;sup>1</sup> Thomsen, Julius; Poggendorft's Annalen, XXV., page 348.

<sup>&</sup>lt;sup>8</sup> Nichols, E. F., PHYSICAL REVIEW, Vol. I., p. 1.

ity of the water cell by means of a cell containing a solution of iodine in carbon bisulphide.

Evidence of the inadequacy of the correction obtained by this method and consequently of the inaccuracy of all our data, for the radiant efficiency of artificial light sources, that have been obtained by the method of the water cell has recently been afforded by Ångström.<sup>1</sup> He determined the radiant efficiency of the acetylene flame by an ingenious method in which the infra-red radiation is separated from the light-giving rays by the interposition of an opaque screen in the spectrum, after which the light is reassembled and its energy compared with the total energy from the flame. Ångström found for the radiant efficiency by this entirely independent method the value .056 which is a little more than half as great as that obtained by Stewart and Hoxie with a similar flame by the use of the water and iodine cells.<sup>2</sup> He finds that all radiant efficiencies hitherto published, with the possible exception of those given by Langley,<sup>3</sup> who made use of the method of plotting the energy curve for a source of light and of integrating the areas of the luminous and non-luminous portions, are much too large.

A recent investigation by one of the present writers ' of the infra-red spectrum of iodine both in the solid form and in solution shows conclusively that the assumption upon which the use of iodine solutions for the purpose of determining the correction which it is necessary to apply to the infra-red radiation transmitted by the water-cell, namely, that iodine solutions which are of sufficient concentration to absorb completely the rays of the visible spectrum are fully transparent in the infra-red, is unwarranted. It is our purpose in the present paper to determine as definitely as possible the degree of inaccuracy involved in the usual method of measuring radiant efficiencies; and with this end in view we have made the following measurements.

RADIANT EFFICIENCY BY THE METHOD OF THE WATER CELL. A cylindrical acetylene flame from a single-tipped burner was

window was noted when exposed to the direct radiation of this flame; also when a water cell with thin glass walls and containing a layer of distilled water I cm. in thickness was interposed; and finally when an iodine cell was placed behind the water cell so that the rays had to pass through the two. The iodine cell was of the same dimensions as the water cell. It contained a solution of iodine in carbon bisulphide of such concentration that the filament of an incandescent lamp viewed through the cell was just on the point of extinction. The result of five series of readings was as follows :

Deflections (Direct).	Deflections (Through Water Cell).	Deflections (Through Both Cells)
15.40	2.29	0.98
15.25	2.30	1.00
15.35	2.29	0.99
15.22	2.29	1.03
15.28	2.36	1.00
15.300 (mean)	2.306 (mean)	1.000 (mean)

TABLE	I.

The energy transmitted by the water cell according to the above data is 2.306/15.300 = .1507.

The proportion of radiation passing both cells as compared with that of passing the water cell alone is 1.00/2.306 = .4337.

The radiant efficiency of the flame computed in the usual manner would be  $.1507 \times (1 - 0.4337) = .086$ . This value is somewhat lower than that obtained by Stewart & Hoxie (.105) for a flame of the Naphey type. That the flame of burners of the Naphey type is in general whiter than the flame from the single-tipped burner and presumably therefore is of a higher temperature and of a somewhat higher radiant efficiency, has already been shown by means of a spectrophotometric examination of these flames.<sup>1</sup>

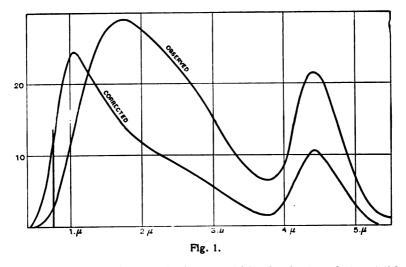
RADIANT EFFICIENCY BY INTEGRATION OF THE ENERGY CURVE.

The energy curve of the spectrum of the flame was obtained by using a mirror spectrometer with rock-salt prism. and measuring Nichols radiometer. This curve of observed intensities was corrected for slit-width variations by means of Paschen's equation :

$$af(x) = F(x) - \frac{1}{6}F_1(x).$$

A further correction was likewise introduced on account of the selective character of the transmission by the rock-salt window which was found to be much less transparent for the shorter than for the longer wave-lengths.

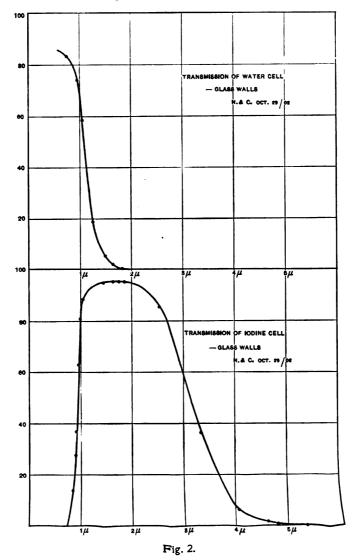
In making these measurements of the spectrum a set of three readings was obtained for each of a series of wave-lengths, one reading for the total intensity of the spectrum at the point in question, one for the radiation transmitted through the water cell and one for the radiation transmitted through the iodine cell; these being placed separately and successively between the flame and the spectrometer slit. The curve of intensities when no cell was interposed is plotted both in the observed and corrected form in Fig. 1.



In this diagram the area included within the limits of the visible

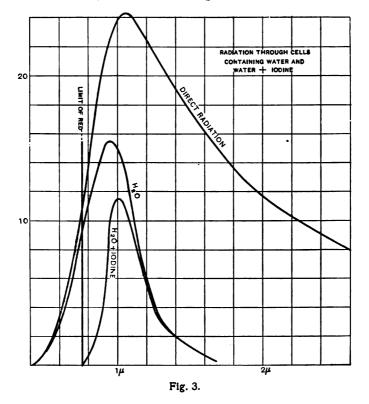
TRANSMISSION THROUGH WATER AND IODINE.

The transmission of the water cell and of the iodine cell computed from the readings described above is shown in Fig. 2, in



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It will be seen that the water cell, so far from being opaque throughout the infra-red, transmits 67 per cent. at wave-length 1  $\mu$ and becomes completely opaque only when wave-length 1.8 is reached. The iodine cell, the function of which in the determination of radiant efficiency, is based upon the assumption that it will transmit whatever infra-red radiation may pass through the water cell, is likewise very far from fulfilling this condition : for although



the transition from opacity to transparency is very rapid, the solution does not become fully transparent until the region 1.5  $\mu$  is reached.

The precise significance of the data obtained by the water cell method and the complete failure of the iodine cell to serve as a means shown by the curve marked  $H_2O$  and that portion of the energy thus transmitted which gets through the iodine cell when the latter is placed behind the water cell is shown by the curve marked  $H_2O$  + *iodine*. These curves indicate clearly the very large error involved in the use of the iodine cell and lead us to the rejection of it altogether in the study of radiant efficiencies.

An integration of the area of luminous energy and of the total energy enclosed in the curve marked H<sub>a</sub>O shows that of the energy transmitted by the water cell only about one sixth, more accurately 0.174, falls within the visible spectrum. A comparison of the area measuring the luminous energy transmitted by the water cell with the area representing the total luminous energy of the flame shows that the losses of luminous energy by reflection and transmission in passing through this cell amount to 13 per cent. In order to check this ratio, the precise determination of which with the radiometer is somewhat precarious on account of the small deflections obtained in the visible spectrum, two similar acetylene flames were mounted at the end of a photometer bar and the ratio of their intensities was determined. The water cell was then placed in front of one of them and the measurement repeated. The transparency of the water cell thus measured was found to be 0.87, a value which is in agreement with that obtained by the integration of the curves. The computation of the radiant efficiency of the flame from the data obtained by the integration of these curves gives us  $.1507 \times$ .174/.87 = .030; a value somewhat smaller than that obtained from the integration of the energy curve itself.

Both of these values for the radiant efficiency are surprisingly low. The method of integrating the energy curve for the determination of the ratio of luminous energy to the total area, while it appears at first sight to be the most direct and therefore likely to give the best value, is unfortunately subject to considerable errors arising from the difficulty of making the proper correction for variations of slit-width within the luminous area. The radiometer readings for this portion of the spectrum are always small and the change in the slit-width, measured in wave-lengths, undergoes its most rapid changes as we pass over from the visible to the invisible spectrum. Uncertainties concerning the trend of the dispersion

curve of the prism which are apparently insignificant affect the ordinates of the corrected energy curve in this region very notably. Fortunately we have the means of checking the accuracy of the results in this case by comparing the ratio of the area of the curve representing the total transmission of the water cell to that of the total area of the energy curve with the corresponding ratio obtained from the measurement of the deflections due to the unrestricted and undispersed radiation from the flame as compared with the deflections produced when the water cell was interposed in the path of the rays. The ratio of the areas by integration is 1.528 while that obtained by the latter method is, as we have already seen. 1.507. The close agreement of these ratios is such as to give confidence in the substantial accuracy of the two methods.

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An explanation of the low value of the efficiency of this flame is to be found in the peculiar character of its energy curve. It will be noted that the emission band at  $4.4 \mu$  is very large. The area of the region lying between  $4.0 \mu$  and  $4.9 \mu$  is in point of fact .192 of the total area of the curve. Integration of the corresponding area of a curve for a cylindrical flame measured by G. W. Stewart and corrected by Paschen's equation shows for the corresponding region an area of .0948 as compared with the total area of that curve. The radiant efficiency of Stewart's flame as determined by integration of the luminous and total areas gives .040.

The existence of a very powerful emission band at wave-length  $4.4\mu$  is characteristic of flames of the Bunsen type; as may be seen from the curve given by Stewart<sup>1</sup> in his paper on the spectrum of the acetylene flame. The very large emission band at this wave-length, in the case of the flame upon which the measurements described in the present paper were made, probably indicates that the air ducts in the burner were too large as compared with the orifice through which the acetylene gas reached the tip.

A reduction in the supply of acetylene from partial clogging of the orifice would tend to convert the flame into the Bunsen type and to reduce its radiant efficiency. Measurements of the spectrum The ratio of the deflection at the top of this band to that at the maximum of the energy curve on April 26 was .40. On October 29, the day of the readings from which the curve shown in Fig. 1 was plotted, it was .76. On November 8 it was .50; on December 13 it was .59.

Measurements with the water cell at a time when this ratio had a value of .50 gave for the ratio of the transmitted to the direct radiation .200 as against the .150 of Table I. The radiant efficiency on that day, assuming the ratio for luminous to total transmission through the water cell not to be appreciably changed, was  $.174 \times .20/.87 = .040$ . This value is identical with that obtained by integration of the curve for Stewart's flame.

We have in these observations without doubt an explanation of the principal difficulty of using the acetylene flame as a primary standard in photometry. The gas orifice in all existing types of the acetylene burner is very small and the partial clogging of this orifice would serve to modify to a serious extent the quality and the total brightness of the flame.

#### CONCLUSIONS.

The observations recorded in this paper suffice to show the very large correction which must be applied to the ratio between the energy transmitted by a water cell and the total radiation if one is to obtain a correct value for the radiant efficiency of any source of light; also the futility of the method of ascertaining this correction by means of the iodine cell. It is obvious that the factor by which this ratio must be multiplied will vary with the radiant efficiency, and while the nature of this variation is perhaps comparatively simple in the case of sources in which the light is derived from incandescent carbon the value of the correction for other sources can only be ascertained when we have definite information concerning the character of the infra-red spectrum. Were we to apply, to take an extreme case, the method of the water cell to the radiation from sodium vapor at the temperature of the electric arc we should have to do with an infra red spectrum nearly all of the energy of which lies, according to the curves published by Snow,<sup>1</sup> at wave-lengths less than 1.4  $\mu$ . The infra-red spectrum of this vapor consists chiefly of

<sup>1</sup> Snow, PHYSICAL REVIEW, Vol. I., p 95.

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two strong lines or pairs of lines at .82  $\mu$  and 1.13  $\mu$ . There is, it is true, a group of lines or bands lying between 1.7  $\mu$  and 1.9  $\mu$  but the energy of these is insignificant. What may lie beyond  $2\mu$  we do not know. A very large part of the energy of such a source of light would presumably be transmitted by the water cell. In the case of the Arons mercury lamp according to measurements reported elsewhere by Coblentz and Geer<sup>1</sup> we have in the infra-red a group of lines which lie within the region of transparency of the water cell and a second group to which the cell would be entirely In the study of such sources of light determinations of the opaque. energy transmitted by the water cell are without significance. Results obtained by exploring the entire spectrum and plotting the energy curve would, on account of the difficulty of making a satisfactory correction for the variations of slit width, likewise be of doubtful value. To determine the radiant efficiency of such sources we must have recourse to a method based upon the principles used by Angström in his recent paper or we must find some screen which will be opaque to the entire infra-red, and the transmitting power of which for the visible spectrum can be determined photometrically.

PHYSICAL LABORATORY OF CORNELL UNIVERSITY,

December 24, 1902.

<sup>1</sup>Coblentz and Geer, PHYSICAL REVIEW, Vol. XVI., p. 279.

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STEFAN'S LAW.

# NOTE ON THE DEDUCTION OF STEFAN'S LAW.

#### BY EDGAR BUCKINGHAM.

BOLTZMANN'S thermodynamic deduction of Stefan's law, that the total temperature radiation of a black body is proportional to the fourth power of the absolute temperature, is very concise; and it seems to me that the same thing may be done a little more clearly, at least for those who are familiar with the free energy principle.

Starting with the two laws of thermodynamics,

(1) 
$$\delta \varepsilon = \delta Q + \delta W,$$

(2) 
$$\delta \eta = \frac{\delta Q}{\theta},$$

we have, for reversible processes,

(3) 
$$\delta \varepsilon = \theta \delta \eta + \Sigma X \delta x,$$

where  $\epsilon = \text{internal energy}$ ,  $\eta = \text{entropy}$ ,  $\theta = \text{absolute tempera$  $ture}$ ,  $\delta Q = \text{heat added to the system}$ ,  $\delta W = \text{work done on the system}$ , and  $X_{\kappa} \delta x_{\kappa} = \text{the part of the work due to the increase in the variable } x_{\kappa}$ . If the system has only two degrees of freedom, and the only external force is a pressure, equation (3) takes the familiar form

(4) 
$$\delta \varepsilon = \theta \delta \eta - p \delta v.$$

Let

(5) 
$$\psi = \varepsilon - \theta \eta$$

Then

(6)  $\delta \psi = -\eta \delta \theta - p \delta v.$ 

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EDGAR BUCKINGHAM. [Vol. XVII.

*i. e.*, the work done on the system by the pressure p, during an increase of volume  $\partial v$ , is equal to the increase of  $\psi$ .

The function  $\psi$  is Helmholtz's "free energy," and equation (7) may be read : "The work done by a system during an isothermal, reversible change of state, is equal to the decrease of its free energy." This "free energy principle" is generally expressed simply by the equation which defines  $\psi$ , namely,

(8) 
$$\psi = \varepsilon - \theta \eta,$$

which is then to be read: "The decrease of the free energy of any system during a reversible, isothermal change of state, is equal to the decrease of the total energy, minus its absolute temperature multiplied by the decrease in its entropy."

From equation (6) it is evident that

(9) 
$$-\eta = \frac{\partial \psi}{\partial \theta},$$

so that (8) may be written in the familiar form

(10) 
$$\psi = \varepsilon + \theta \frac{\partial \psi}{\partial \theta},$$

the interpretation in words being similar to that given above. So much for our thermodynamic tools.

The assumption to be made in the deduction of Stefan's law is one drawn from the electromagnetic theory of light; namely, that parallel rays falling on a black surface exert on it a pressure equal to  $\varphi$ , the volume density of energy in the incident beam. For an entirely unordered radiation inside a black enclosure of absolute temperature  $\theta$ , the pressure at any point of the bounding surface will then be  $\frac{1}{3}\varphi$ ; just as in the kinetic theory of gases we imagine our molecules, for simplicity, divided into three groups moving at right angles, each group having the sum total of the components

uniform temperature of the walls be  $\theta$ , and let the density of the unordered radiation inside be  $\varphi$ . Let the piston move out, reversibly and isothermally, so that the volume increases by  $\delta v$ . The work done by the system is

$$(11) \qquad \qquad p\delta v = \frac{1}{3}\varphi \delta v,$$

which is, accordingly, the decrease in the free energy of the system, or the  $\psi$  of equation (10). We therefore have

(12) 
$$\frac{\partial \psi}{\partial \theta} = \frac{1}{8} \frac{\partial \varphi}{\partial \theta} \, \delta v,$$

 $\delta v$  being arbitrary and independent of  $\theta$ .

The temperature having been kept constant, the density of energy has not changed. Therefore, a quantity of energy  $\varphi \delta v$  is now inside the enclosure, in addition to what was there at first. The internal energy of the system has, therefore, *decreased* by  $(-\varphi \delta v)$ , which is, therefore, the value of the second term in equation (10). Substituting these values in equation (10), we at once get the equation

$$\frac{1}{3}\varphi \partial v = -\varphi \partial v + \frac{1}{3}\theta \frac{\partial \varphi}{\partial \theta} \, \delta v,$$

2...

or

From this we have, at once,

and

(14) 
$$\varphi = C\theta^4.$$

Those who do not like the free energy principle, may get the result by using the familiar thermodynamic relation

 $\frac{d\varphi}{c} = 4 \frac{d\theta}{\theta},$ 

(15) 
$$\left(\frac{\partial \eta}{\partial v}\right)_{\theta} = \left(\frac{\partial \rho}{\partial \theta}\right)_{\theta},$$

which is evident from equation (6). The heat added to the system during the change of volume is equal to the increase of the internal energy  $\varphi \delta v$ , plus the work which the system has given out, namely  $p\delta v$ , or  $\frac{1}{\delta}\varphi\delta v$ . Therefore, during the isothermal change, the total amount of heat added has been

 $\delta Q = \frac{4}{8}\varphi \delta v;$ 

whence

$$\delta\eta = \frac{\delta Q}{\theta} = \frac{4}{8} \frac{\varphi}{\theta} \, \delta v,$$

and

•

(16) 
$$\left(\frac{\partial \eta}{\partial v}\right)_{\theta} = \frac{4}{8}\frac{\varphi}{\theta}$$

Also, since  $p = \frac{1}{2}\varphi$ , we have

(17) 
$$\begin{pmatrix} \frac{\partial \varphi}{\partial \theta} \end{pmatrix}_{\cdot} = \frac{1}{2} \begin{pmatrix} \frac{\partial \varphi}{\partial \theta} \end{pmatrix}_{\cdot}$$

Substituting in (15) we have

(18) 
$$\frac{1}{8}\frac{\partial\varphi}{\partial\theta} = \frac{4}{8}\frac{\varphi}{\theta},$$

whence

and  

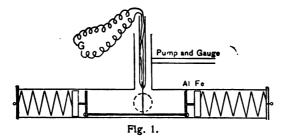
$$\frac{d\varphi}{\varphi} = 4 \frac{d\theta}{\theta},$$
(19)  
as before.  

$$\varphi = C\theta^4,$$

# THE DISTRIBUTION OF MOTION IN A CONDUCTING GAS.

### P. G. NUTTING.

WHEN a rarefied gas is conducting an electric current we have every reason to suppose that there is a departure from the uniformly distributed motion assumed by the kinetic theory. The motion of the charged particles constituting the current must be largely longitudinal but, except at very low pressures, this motion must be more or less interfered with by collisions with neutral particles. In any case if we attempt to ascertain the temperature of the gas by inserting in it a flat bolometer strip or thermopile, the temperature which this will acquire will depend upon its orientation with respect to the stream lines. Hence the word temperature applied to a conducting gas is ambiguous if not meaningless unless we at least specify it as longitudinal or transverse



meaning by these terms the minimum and maximum temperatures indicated by a flat detector as its orientation is varied. In the present investigation a very thin, wide thermopile was inserted in various parts of the discharge through a wide range of pressures and current densities.

The discharge tube was designed to give as nearly as possible the normal, one dimensional discharge. A straight tube 60 cm. long and 3 cm. in diameter was fitted at its center with a side tube provided with a ground-glass stopper. Through this stopper were inP. G. NUTTING.

serted a glass tube supporting the thermopile and the lead wires to the same. By turning the stopper the pile could be set lengthwise or transversely in the discharge. The ground joint held the lowest vacua without trouble but to turn easily, it required to be occasionally opened and regreased. Both electrodes were of aluminium and were backed with a thick disk of soft iron. They were connected together by a thin glass rod at one edge and to the ends of the tube by spirals of thin copper wire so that the whole system could be moved past the thermopile by means of a magnet. A d'Arsonval galvanometer was used in connection with the thermopile. To measure the current through the tube a Weston millivoltmeter was connected in series. This instrument had a resistance of 8.851 ohms so that the currents quoted are too large by that factor.

Current was supplied by a gang of 500-volt, direct-current dynamos connected in series. Eight, sixteen or twenty-four of these were used but eight of them giving 4,000 volts were found to be ample and more easily controlled. 12,000 volts continuous leaks badly over wood, into the air and across switches. The current was controlled by a cadmium iodide in amyl alcohol fluid resistance.

Thermopiles of several different sizes were used, but all gave practically the same readings under the same conditions, showing that the heating effect was proportional to the area exposed. Fine iron and copper wires were twisted together at the ends, hammered flat, inserted between two disks of copper foil and lightly soldered. The largest pile was about 0.2 mm. thick and 14 mm. diameter. One degree corrresponded to about 2 mm. on the scale. Temperatures of over 100 degrees were recorded with the pile across the tube in a cathode ray discharge.

In calculating the relative heating effects from the temperatures attained, slight losses by convection and conduction were neglected and the law of emission for black bodies,  $E = A \lambda^{-n} e^{-B/\lambda \tau}$ , supposed to hold for the pile. The integral of this is  $A B^{1-n} \Gamma(n-1) T^{n-1}$ .

ometer deflections were taken as proportional to the energy received. A specimen set of readings is given below; they were taken at a pressure of 0.063 mm. with the pile in the middle of a cathode dark space 16 mm. long. The subscript, indicates that the pile is across the tube,  $_{\prime\prime}$  that it is placed lengthwise.

	6	c	6		Deflections		Ratio
2	<i>S</i> ,,	<i>S</i> <b>_</b>	S <sub>0</sub>	D,,	D	Ratio.	$\Delta T^{4}$
5.0	38.03	36.33	39.40	1.37	3.07	2.24	2.57
10.0	36.98	29.28	39.25	2.27	9.97	4.39	5.60
15.0	35.25	26.48	39.02	3.77	12.54	3.33	4.00
20.0	33.60	24.61	38.50	4.90	13.89	2.84	3.36

When the pressure is greater the energy received by the pile in the two positions is more nearly equal, the ratio being only about 1.2 at a pressure of 1 mm. At lower pressures the ratio is greater, for instance at a pressure of 0.015 mm. a ratio of 12 was obtained. In all cases the ratio was found to be a maximum for a moderate value of the current, being much less when the current is either very great or very small.

Outside the dark space in the cathode glow at the same current and pressure, the heating effect with the pile lengthwise in the tube is much greater than in the dark space, while with the pile across the tube it is somewhat less, indicating that the proportion of longitudinal motion is much less. Farther out in the glow the ratio is still less and in the Faraday dark space is practically unity, indicating that here the motion resembles that in a gas not carrying current. In the anode glow the discharge was disturbed by the presence of the pile so that no observations of value were obtained. Connecting the pile and galvanometer to earth appeared to have no effect on the heating of the pile. Charging them positively or negatively with an electric machine appeared to produce no effect, but the galvanometer was so disturbed that the results are uncertain.

As to the mechanism of the discharge, it appears as though the conducting particles were projected normally through the cathode dark space all in nearly paralled paths with about the same velocity. The inert gas appears to be driven back bodily as far as the end of the dark space and the beginning of the cathode glow. Within the glow, apparently the motion is gradually reduced by collisions to the completely irregular gas motion in the Faraday dark space.

In confirmation of these tentative hypotheses these additional observations may be cited: (1) The width of the dark space is independent of the current strength. Over a range of current from three to seventy the dark space was found not to vary by one per cent. if at all. Increasing the current merely sets more particles in motion with the same velocity. (2) The heating effect on the transverse thermopile in the cathode dark space is directly proportional to the current. (3) Except for small currents and large pressures (in which case it is one-sided) the cathode dark space and cathode glow are symmetrical about a symmetrical cathode, indicating that the charged particles are shot off rather than merely moving along a fall of potential. (4) When by a very slight increase in the current, the discharge is made to change suddenly from the single to the double form, there is no corresponding change in the heating effect. It may be mentioned that it was found impossible at any current or pressure to produce a doubling of the anode discharge as though the positively charged particles were too heavy to be projected off and mercly followed the fall of potential. The canal ray glow within the cathode dark space does not extend both ways as though caused by the impact of particles coming from the direction of the anode.

Now the projecting of the changed particles from the electrodes imparts energy to the electrodes themselves, perhaps an amount equal to that given the flying particles. Whether this energy is given the electrodes mechanically or in some unknown way by the mere transfer of the electricity from the metal to the gas particles, it is not easy to decide but the amount of the energy was easily measured. The thermopile was merely made the electrode and earthed. Except at low cathode ray vacua the heating of both anode and cathode was found to be independent of the pressure and directly proportional to the current. Even when the cathode rays were very strong, if they were deflected by a magnet, the heating of the anode was found to be still independent of the pressure and proportional to the current. The heating of anode and cathode were found to be about equal and equal to the heating of No. 4.]

the pile in the normal cathode dark space at the same pressure and current but the results were not sufficiently accurate to establish this relation. The measurement of electrode heating would appear to be a most fruitful method of attacking the problem of gas conduction once the relation of the heating to the nature of the electrodes and the gas used has been determined.

CORNELL UNIVERSITY, June, 1903.



# SOME FURTHER EXPERIMENTS WITH THE COHERER.

#### BY PHILIP ELY ROBINSON.

THE two experiments herein described were suggested by my previous work<sup>1</sup> on the coherer. In the former experiments a linear receiver was employed, which contained a single contact coherer, and whose total length was 50 cm. The experiments on resonance showed that the half wave-length of this receiver was 49.5 cm. An application of the theory of the Hertzian oscillator to the receiver indicated that the coherer had a capacity of 40 cm.<sup>2</sup> (in electrostatic units). A new receiver of almost double the former length was set up for these experiments. The first investigation consisted in determining its half wave-length, whence the capacity of the new coherer could be compared with that of the former one. Again in the investigation of the coherer with a direct current it was noticed on applying to the coherer ends a potential difference greater than the critical potential difference that the resistance of the coherer seemed to fall instantaneously to a certain value which was termed impulse value (" Sturzwert ")<sup>2</sup> and then to fall slowly further until the relation of the resistance of the coherer to the resistance in the circuit with it was such that the resulting potential difference at the coherer ends had taken on a definite value, which was called the cquilibrium potential difference. The second investigation is concerned with these impulse values, the object being to determine whether they have a definite value depending upon the applied potential difference, and if so, to see what relation exists between Some work along this line has already been done by the two. Ketterer.<sup>2</sup>

<sup>1</sup> "Der elektrische Widerstand loser Kontakte und seine Anwendung in der drahtlosen Telegraphie," Inaugural-Dissertation. Leipzig: J. A. Barth, 1903. Ann. d. Ph., 11, p. 754, 1903.

### I. RESONANCE.

The receiver used consisted of two straight pieces of copper wire 2.13 mm. in diameter, which carried at one end short steel caps of the same diameter. The total length of each piece including the The ends of the steel caps were spherical steel cap was 40.2 cm. (radius about  $2 \text{ mm.}^1$ ). These rods were suspended by silk threads from a long glass tube. The steel caps, their spherical surfaces pressing slightly against each other, formed the single contact coherer. Connections with the rest of the circuit were made by short pieces of wire which projected into mercury cups precisely as in the former experiments. Just as formerly a simple Hertzian oscillator was employed. The responsiveness of the coherer or receiver to each wave-length emitted by the oscillator was determined by the resulting resistance of the coherer, a smaller resistance indicating a

150 cm.	98.4 cm.	97.9 cm.	97.4 cm.	96.9 cm.	75 cm.
1.34	1.50	1.40	1.09	1.40	2.71
2.38	1.37	1.13	1.10	1.37	1.51
2.16	1.29	1.43	1.14	1.54	2.25
1.14	1.00	1.37	1.12	1.51	2.18
1.24	1.16	1.29	1.14	1.33	1.83
2.14	1.58	1.33	.93	1.50	2.75
1.70	1.11	1.33	.88	1.17	2.84
2.15	1.42	1.34	.98	1.37	
1.72	1.07	1.32	1.10	1.31	
1.12	1.29	1.38	1.13	1.50	:
ean 1.71	1.28	1.33	1.06	1.40	2.15

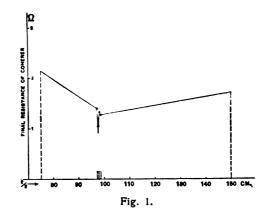
Half Wave-lengths. Final Resistances of Coherer in Ohn	Half	Wave-lengths.	Final Resistances of	f Coherer in Ohms
--	------	---------------	----------------------	-------------------

greater responsiveness. The coherer was found to fatigue very quickly, and when fatigued the values of the final resistance for a given wave-length became larger and more irregular. To bring the coherer back to its *fresh* or *sensitive* condition, which was effected by repolishing the contact surfaces, was very difficult. Accordingly numerous determinations of the final resistance for each wave-length were made, and the mean of the ten lowest, (in one case of the seven lowest), was taken as the measure of the responsiveness for that

<sup>1</sup> The former experiments showed that the curvature of the contact surfaces does not influence the capacity nor the critical potential difference of the coherer.

particular wave-length. To show the degree of regularity these determinations are given in full.

Plotting these results as a curve where the ordinates are mean



final resistances and the abscissas half wave-lengths, the following curve results.

This curve is precisely similar to that found under similar circumstances in the former experiments (compare Curve I., p. 47). The minimum lies at 97.4 cm., that is, the half wave-length of the receiver is 97.4 cm. Applying the formula

$$\frac{2\pi(l_1+\lambda/4)}{\lambda} lg \frac{2\pi(l_1+\lambda/4)}{\lambda} = \frac{l_1+\lambda/4}{4Clog d/R}$$

employed in my former paper (p. 49), and substituting the values :

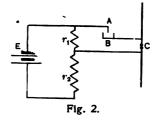
 $\lambda = 194.8$  cm.,  $l_1 = 49.2$  cm., d = 98.4 cm., and R = 0.106 mm.,

the resulting value of the capacity C of the coherer is 70.4 cm. as against 40 cm. in the previous experiments. Had the capacity been 40 cm. in these experiments, the resulting half wave-length would have been, according to the formula above, 96.7 cm., a result which lies outside the limit of error. On the other hand, had the capacity of the coherer in the former experiments been 70.4 cm., the half wave-length of the receiver would have been 49.7 cm., which lies well within the limit of error there. Consequently one is not able to conclude that the capacity in the two cases was really different. Further light will be thrown on this point by the experiments of F. Hodson, an account of which will appear shortly.

## 2. INVESTIGATION OF IMPULSE VALUES.

The method of investigation consisted in applying for an instant to the coherer ends a potential difference greater than the critical potential difference. The resulting resistance of the coherer would then be measured under a low voltage. The method of applying the desired potential difference is indicated in the accompanying figure. The battery E of storage cells of measured voltage was closed through the resistances  $r_1$  and  $r_2$  (usually  $r_1 = r_2 = 100 \Omega$ ). From the ends

of  $r_1$  wires lead off to the coherer C, one being connected to one end of the latter, while the end A of the other would be dipped for an instant into the mercury cup B which was in connection with the other end of the coherer. In this way the fraction  $r_1/(r_1 + r_2)$  of the



voltage of the battery E would be applied to the coherer ends, provided the resistance of the coherer was large compared to  $r_1$ , and that the effect of the self induction of the circuit be disregarded. The resistance of the coherer was quite large compared to  $r_1$ , and the circuit was so arranged that its self induction was small, so that errors due to these causes were neglected. Another arrangement, which it is not necessary to describe here, was employed to measure the resistance of the coherer.

The results showed that to each applied potential difference there corresponded a definite final resistance or impulse value. Fatigue of the coherer was very manifest in these experiments, and the difficulty in keeping the coherer at the same sensitiveness prevented me in the limited time at my disposal from getting a series of measurements for the coherer at the same sensitiveness throughout. The results are divided into three sets, which evidently corresponded to different sensitivenesses.

From the first and second columns one or two results which were apparently abnormally low are excluded, and from all columns large results evidently due to fatigue are omitted. P. E. ROBINSON.

[VOL. XVII.

It was noticed in the course of the experiments that the regularity of the results increased markedly as the applied potential difference became greater. Second, that *the greater the applied voltage, the smaller is the impulse value of the coherer resistance.* The relation between the two is evidently not a linear one. Third, the greater the sensitiveness of the coherer the smaller is the impulse value of the coherer resistance for the same applied voltage.

5.3	4.25	2.94	2.00	1.55	1.01	3.02	9.12	1.04 V
1.17	2.20	1.62	3.90	7.07	15.2	6.60	8.40	52.6 Q
1.2	2.30	1.44	4.31	6.47	20.4	5.00	8.40	46.3
	1.71	1.50	3.79	5.34	21.2	4.84	6.26	47.8
	1.82	1.56	4.11	7.00	17.2	6.66	7.11	51.7
ì	2.20	1.48	4.18	5.51	.	7.90	6.17	37.6
1	2.30	1.47	3.96	6.75		7.65	6.19	50.0
!	2.04	1.52	3.93	5.95	i i	4.37	8.73	37.0
	1.90	1.50	4.41	6.37	1	5.30	7.23	41.1
		1.61	4.32	6.51	1	4.89	7.25	53.4
1		1.63	3.60	6.65		6.05	7.66	46.1
1		1.28	3.70	5.46		1		43.1
1		1.54	, i		1	,		51.3
1.1	2.06	1.51	4.02	6.28	18.5	5.93	7.70	46.5
n valu	Mear							

Applied Potential Differences in Volts. Impulsive Values in Ohms.

If, as I believe, the value to which the coherer resistance falls when acted upon by electric waves corresponds to an impulse value, then by comparing the value produced by electric waves with the impulse values, we should be able to measure the potential difference initially set up at the coherer ends by the electric waves, provided the sensitiveness of the coherer be the same in both cases. Thus comparing the impulse values given above with the values of the final resistances given in the first part of this paper, we are lead to conclude that in the experiments on resonance the waves from the 5 m. distant oscillator set up at the coherer ends a potential difference which in every case was greater than 2 volts and which probably was over 3 volts.

In my former experiments fatigue of the coherer had only been called forth by electric radiations. These experiments showed that fatigue can also be called forth by a direct current. The ap-

plied voltages were such that it was not impossible for a spark discharge to occur between the coherer ends. The suggestion offered in my former paper that the fatigue may be caused by such a spark, which would increase the density of the layer of oxide on the contact surfaces of the coherer, would then still be applicable. This subject of fatigue I hope shortly to investigate further.

In conclusion I wish to thank Professor Michelson for placing the facilities of the Ryerson Physical Laboratory at my disposal.

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UNIVERSITY OF CHICAGO, June 3, 1903.

## MAGNETIC DOUBLE REFRACTION.<sup>1</sup>

### BY ARTHUR W. EWELL.

D<sup>R.</sup> QUIRINO MAJORANA<sup>2</sup> has shown that certain specimens of dialyzed iron (a colloidal solution of peroxide of iron) become double refracting in a magnetic field, the optic axis having the direction of the magnetic lines of force.

It seemed to the author of interest to repeat Majorana's experiments with such specimens of dialyzed iron as could be obtained locally, to use an alternating magnetic field and to test other substances with a very sensitive apparatus for detecting double refraction, suggested by Lord Rayleigh.<sup>3</sup>

A magnet suitable for alternating currents was constructed by replacing the laminations of one of the shorter sides of the core of a five-kilowatt, core-type transformer, by laminations cut to give an air gap of 0.5 cm. between faces I cm. wide and 12.5 cm. long, outside of which the laminations were cut obliquely to concentrate the field. The core was wound with 86 turns of No. 2 cable which was calculated to give the maximum field with an alternating current of 60 amperes at 220 volts. The magnet was calibrated for direct currents by withdrawing from between the poles an exploring coil connected with a ballistic galvanometer with which it had been calibrated and for alternating currents, from the E.M.F., measured with a low reading a. c. voltmeter, induced in the same coil in the air gap.

<sup>1</sup> When this article was in type I became acquainted with the second paper by August Schmauss in No. 9 of this year's volume of Annalen der Physik, in which he describes the temperature reversal and more fully than I the behavior of glycerine and jelly solutions, and plausibly develops the theory that the phenomena are due to the solutions consisting of minute particles in suspension in a medium of different and differently varying permeability.

<sup>8</sup> Academia dei Lincei, Rendiconti ; 1902, X., pp. 374, 463, 531, XI., pp. 90, 131.

## No. 5.] MAGNETIC DOUBLE REFRACTION.

The liquid tested was contained in a trough with plate-glass ends which fitted into the horizontal air gap. The source of light was a three-glower 150 c. p. Nernst lamp, with the filaments vertical and the plane of the filaments oblique to give the equivalent of a very brilliant band of light of nearly the width of the air gap. Between the lamp and the magnet was a Nicol set at 45° to the magnetic field. On the other side of the magnet was a horizontal strained glass plate, in front of which was a Nicol, crossed with reference to the first, and finally a short-focus telescope. The strained glass plate was 0.28 cm. thick, 30 cm. long and 3.3 cm. broad. It rested edgewise on supports, near the middle, 3 cm. apart and the ends were pulled down by rubber bands towards the base on which these supports rested. The horizontal dark band, the neutral axis of the bent glass plate, was viewed through the telescope and its location fixed by two silk fibers attached to the glass strip parallel to the edges of the band. If any appreciable double refraction appeared in the air gap the dark band was displaced to a position where this double refraction was neutralized. The sensitiveness of the apparatus was determined from the observation that 100 g. pressure upon a piece of plate glass 2.5 cm. wide gave an appreciable upward movement of the band. According to Mascart,<sup>1</sup> for average crown glass, 10 kilos pressure per mm. width produces a difference of path of  $0.5 \lambda$ . (This value was adopted) by Lord Rayleigh and agrees well with the recent results of F. Pockels.<sup>2</sup>) I could, therefore, detect a difference of path of  $0.0002 \lambda$ . The minimum difference which Dr. Majorana could detect was 0.004  $\lambda$ . The greater sensitiveness of the optical apparatus much more than compensates for the weaker magnet, the maximum field which I could obtain being 7,000 units while Dr. Majorana's was 18,-000. The length of his air gap was 7 cm. Crown glass, subjected to pressure behaves as a negative crystal. As the magnetic lines of force were horizontal an upward movement of the band indicated positive magnetic double refraction.

acted with in a search for very old specimens of dialyzed iron and a number of such specimens were obtained. Several specimens of fresh product and also of intermediate age were also secured. The older specimens gave enormous motion of the dark band, generally negative. Specimens fresh from the preparers gave positive double refraction of a few thousandths  $\lambda$ . Dialyzed iron carefully prepared according to the directions of Dr. Majorana showed no double refraction after ten days' dialysis. Majorana states that his own preparations were uncertain and never very active. Ferrous and ferric chloride gave slight positive double refraction.

The following substances in the densest solutions consistent with sufficient transparency, gave no double refraction : ferrous sulphate, ferric sulphate, iron alum, citrate of iron, tincture of dialyzed iron, eisen zücker, nickel chloride, nitrate and carbonate, colloidal nickel, cobalt sulphate, chloride and nitrate, manganous sulphate and chloride. Water and carbon bisulphide were also inactive.

For quantitative study of the dialyzed iron, the strained glass plate was replaced by a Babinet compensator. Unless otherwise stated the light from the Nernst lamp was filtered through several thicknesses of red glass, giving quite monochromatic light of measured wave-length 6,600 Ångström units. The movement of the wedge to introduce a difference of path of one wave-length of this red light was 15.2 cm.

The double refraction of a specimen of dialyzed iron was found quite definite for a given age, concentration, magnetic field and temperature as is illustrated by the following observations upon a dilution of what will be designated specimen F (over 8 years old), of concentration 1:40 (I c.c. of dialyzed iron to 40 c.c. of water, density equal 1.0033). The figures for the movement of the band are the means of three independent (usually identical) readings and are all negative.

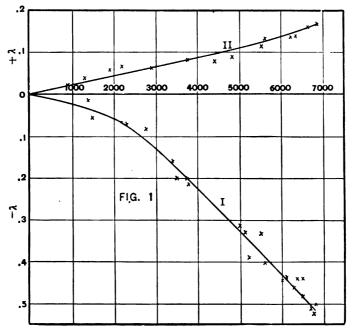
Amperes,	28	33	53	65	86
Movement of band,	1.2	3.2	5	6	7.5

Freshly prepared dilution of same concentration.

Amperes,		38	61	16	49	70	
Movement o	f band,	3	6.4	8.4	4.9	6.6	
Another freshly	prepar	ed dilu	tion upo	on the fo	ollowin	g day.	
Amperes,	15	24	34	48	54	66	76

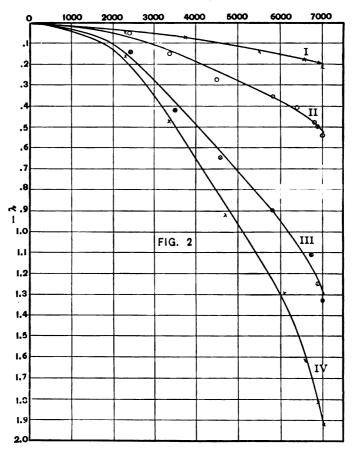
Movement of band, .2 1 2.4 4.7 6 6.9 7.7 These results are plotted in Fig. 1, I., with the strength of field as abscissæ, determined from the current and calibration curve, and as

ordinates, the difference in path, in terms of the wave-length of the red light, obtained by dividing the movement of the bands by 15.2.



In Fig. I, II are plotted observations upon a I:20 dilution of specimen B which was above five years old and which gave the greatest positive double refraction.

Figs. 2 and 3 illustrate the effect of varying the concentration. Fig. 2 represents observations upon specimen M which was at least seven years old and probably much older. The four concentrations were: I., I: 160; II., I: 80; III., I: 40; IV., I: 20. Fig. 3 gives similar observations upon specimen F of concentration: I., I: 80; II. I:40; III.,  $I:20.^1$  Three other specimens gave very similar results. On plotting the logarithms of these observations, curves are obtained which are very nearly straight lines inclined at an angle whose tangent is 2, indicating that the double refraction is proportional to the square of the strength of field. Figs. 2 and 3 show



also that the double refraction is proportional to the concentration for weak concentrations but for denser solutions does not increase in proportion to the concentration.

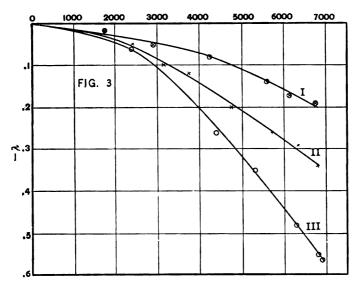
Dr. Majorana concluded that the double refraction was proportional to the concentration but gives none of his observations. He also found the double refraction approximately proportional to the

<sup>1</sup> Fig. 3 represents observations at a higher temperature than Fig. 1.

#### No. 5.] MAGNETIC DOUBLE REFRACTION.

square of the field, extending his observations to the limit of his more powerful magnet.

Dr. Majorana found but two unstable specimens which gave negative double refraction in weak fields. The most active specimens which he studied were positive in weak fields, reversed as the field



increased and for intense fields were strongly negative. I could detect no such reversal in weak fields. Even in fields so weak as to give a barely perceptible movement of the dark band in the Rayleigh apparatus the double refraction was still negative.

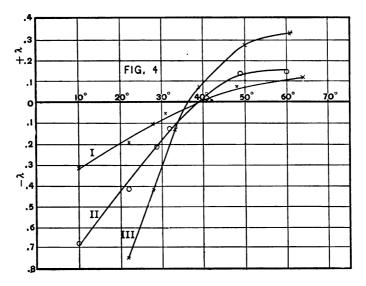
Specimen.	Field.	(d. p.),.	(d. ∳.)g.	$\frac{(d \not p.)_{l}}{(d \cdot \not p.)}$
M 1 : 160	6,800	.27	.38	1.41
"	5,700	.20	.29	1.45
M 1:180	6,800	.48	.64	1.34
"	5,700	.37	.53	1.43
T1:80	6,800	.31	.47	1.52
"	5,700	.24	.35	1.46
C 1 : 80	7,000	.13	.21	1.56

To determine the dispersion of the double refraction observations were made both with the red light and also with a green light of mean measured wave-length 5,300, obtained by filtering the light

through a solution of potassium chromate and copper chloride. The iron solution absorbed all light beyond the green. The movement of the wedge corresponding to a difference of path of one wavelength was 12.9 mm. The final means of a number of observations upon the difference of path for the two wave-lengths are given below.

The quotient of the wave-lengths is 1.22 and the square of this quotient 1.48 which would roughly indicate that the double refraction is inversely proportional to the square of the wave-length which was Dr. Majorana's conclusion.

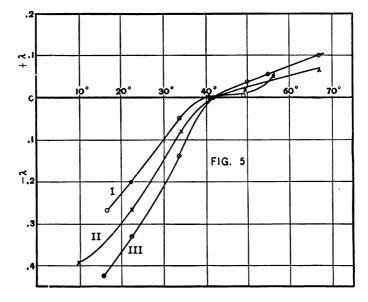
Upon applying alternating currents, for which the magnet was primarily constructed, it was observed that while the double refraction appeared at first, the position of the dark band was less definite



owing to its periodically varying position with the rising and falling field and that with the negatively active solutions, the activity decreased with prolonged application of the current and finally became zero. The cause of this second characteristic was soon found to be the heating of the solution owing to hysteresis in the iron of the magnet and thus being led to a study of the dependence

the temperature is still further raised, they acquire positive activity. Upon cooling, negative activity returns of the same magnitude as before heating.

Fig. 4 gives observations upon three concentrations of specimen F in a field of 6,800 units: I., I:80; II., I:40; III., I:20. Fig. 5 represents observations upon a I:80 dilution of specimen T which was at least five years old; I., red light, field = 5,700; II., red light, field = 6,800; III., green light, field = 6,800. Fig. 6, I., II. and III., are similar observations upon a I:80 dilution of specimen M; I., red light, field = 5,700; II., red light, field = 6,800; III., green light, field = 6,800; III.,



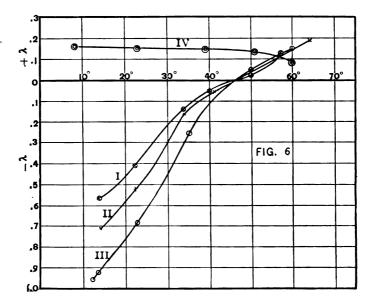
about the same magnitude as at the highest temperatures represented in the figures. All the negative specimens, five in number, behaved similarly.

Positively active specimens showed simply a continuous decrease

A 1:40 solution of F in glycerine was but slightly over half as active as a solution of similar concentration in water. 1 c.c. of F was dissolved in melted jelly composed of 2 grams of calves' foot gelatine to 10 c.c. of water to 10 c.c. of glycerine. As the jelly solidified the activity, measured at intervals in a direct field, decreased, becoming when the jelly was firm but 0.1  $\lambda$  for a length of 2.9 cm.

A mixture of the positive B and strongly negative F might be either positive or negative according to the proportion. A mixture in the proportion of 10:1 was inactive.

Both positive and negative specimens were found paramagnetic by Quincke's manometric method.



Dr. Majorana also discovered magnetic dichroism, i. e., an

unequal absorption of the light components parallel and perpendicular to the field, resulting in certain cases in a rotation of the plane of polarization. The author observed no such effect except in one specimen where there was a slight increased absorption for light polarized perpendicular to the field. Majorana found this dichroism conspicuous only in specimens which showed reversal in weak fields which was not characteristic of any of my specimens.

Dr. Majorana gives two methods for distinguishing active from

inactive specimens :  $1^{\circ}$ , from the appearance in reflected light, the active having a turbid appearance. Some of my active specimens had this appearance and some did not and the same was true of inactive specimens.  $2^{\circ}$ , from the solubility of the precipitate upon adding nitric acid, the greater the insolubility the greater the activity. This rule applied better to my specimens, all those giving a readily soluble precipitate being little active, but when the precipitate was not readily soluble the insolubility was not uniformly proportional to the activity. This partial chemical difference suggested that the active solutions might be St. Gilles' modification of soluble iron oxide, but on preparing the latter it was found inactive.

In general the older a specimen, the greater the activity which was negative in the oldest specimens. Dr. Majorana considers that ferric chloride is eliminated by age. In confirmation, the author found that one drop of concentrated ferric chloride solution in 15 c.c. of F, 1:40, reduced the activity 30 per cent.

I wish to thank Prof. H. B. Smith for very kindly placing at my disposal the extensive facilities of the Electrical Engineering Department.

WORCESTER POLYTECHNIC INSTITUTE, August 1, 1903.

# ENERGY IN THE VISIBLE SPECTRUM OF THE HEFNER STANDARD.

BY KNUT ÅNGSTRÖM.

I. INTRODUCTION.

**T** Is known that the sensitiveness of the eye to light varies with the different wave-lengths and that it is possible to compare with one another only the intensities of sources of light having the same color. We are reduced therefore in photometric researches to the comparison of lights of similar color or indeed when it is a question of spectrophotometric work of intensities in the same spectral region. This gives us, however, no idea of the distribution of energy of radiation in the spectrum since no source of light suitable to serve as a standard has been studied with respect to its distribution of energy. Unfortunately the intensity of radiation in the visible spectrum of our photometric standards is so feeble that although the problem of the distribution of energy in the spectrum has been under consideration for a long time, such a determination has never been made. Nevertheless in the last few years results of the highest importance have been obtained. I shall recall here only the important experimental researches upon the relation between temperature and wave-lengths made by Paschen, Lummer and Pringsheim as well as the no less admirable theoretical developments of Wien, Planck, Lorentz and others. For the infra-red spectrum, in which the intensity of radiation is relatively great, the formulæ established for expressing the relation of the energy to the temperature and to the wave-length have been rigorously tested, but the experimental methods employed thus far have been insufficient for the study of the visible spectrum.

It is, however, of double interest to extend the investigation of

the second place it will then be possible to decide in how far the formulæ established for the radiation of a black body are applicable to the visible spectrum of our ordinary sources in which the light is derived from the radiation of solids.

The object of the present experiments is to contribute to the solution of these questions. The Hefner lamp lends itself well to practical photometry and it is the distribution of energy in this lamp that I have sought to determine. I have attempted also to find the total energy of a radiation of the "bougie-metre" (lux) and to give the energy of its spectral radiation in absolute measure. As a secondary result I have obtained the corresponding values for an electric glow lamp.

Julius Thomsen<sup>1</sup> attempted as early as 1865 to determine the energy of luminous radiation or as it has also been called the mechanical equivalent of light and in 1889 Tumlirz<sup>2</sup> determined the same quantity for the Hefner lamp. He determined the total radiation Q in absolute measure by means of a sort of air thermometer and the luminous radiation L by suppressing the infra-red radiation by absorption in a thick layer of water. This method of separating the luminous radiation from the infra-red, a method which has been employed even in recent times leaves as one may readily comprehend much to be desired, the ratio L/Q between the luminous radiation and the total radiation thus found being too large. The value of L/Q will moreover always to a certain extent remain an arbitrary matter since it depends upon the choice of the boundary between the visible spectrum and the infra-red spectrum. In what follows we shall fix this limit as is commonly done at  $\lambda = 7,600$ (Ångström units) or  $\lambda = 0.76 \ \mu$ .

The Hefner lamp employed is a normal lamp purchased from Siemens and Halske. It is of the form adopted by the Physical Technical Institute at Charlottenburg and is furnished with an arrangement for adjusting the height of the flame. An auxiliary attachment permits of exact control of the different parts of the lamp. The exterior diameter of the tube is 0.82 cm.; the interior diameter 0.8 cm.; its height above the reservoir of the lamp is 3 cm.; and the height of the flame 4 cm. The amyl acetate em-

> <sup>1</sup> Thomsen, J., Pogg. Ann., 125, 348, 1865. <sup>2</sup> Tumlirz, O., Wied. Ann., 38, 640, 1889.

ployed was furnished by the Pharmacy of the University of Upsala. The radiation from this lamp falling upon a surface of I sq. cm., at a distance of one meter, constitutes the unit of illumination or the bougie-metre (lux) examined here.

# II. GENERAL CHARACTER OF THE RADIATION OF THE HEFNER LAMP.

The energy spectra of flames arising from the combustion of the various hydrocarbons all possess essentially the same character. Upon the continuous spectrum of the incandescent particles of carbon are superimposed the spectra of the gaseous products of combustion; that is to say the discontinuous spectra of water vapor and of carbon dioxide. The radiation of the Hefner lamp offers no exception in this respect.

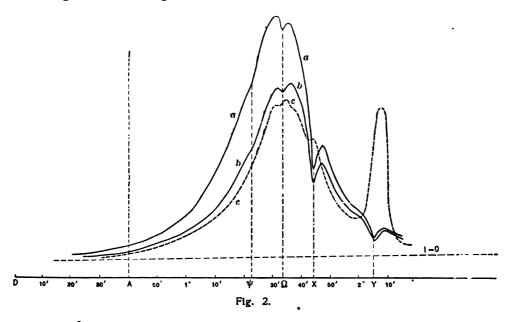
To obtain an idea of the general character of the infra-red spectrum of the Hefner lamp I have made use of the spectro-bolometer with photographic recording device described elsewhere.<sup>1</sup> With this instrument I have recorded the energy of the spectrum of an incandescent lamp; I have compared the same with the continuous spectrum of the Hefner lamp and I have sought to determine the current in the lamp for which the two energy spectra are as nearly

identical as possible. The electric lamp employed for this purpose and in the researches of which I shall give account in what follows came from the Bavarian manufactory of glow lamps in Munich. The filament of this lamp is very thin and is maintained perfectly rigid by another heavier strip of carbon in the form of an arc. Under normal conditions this lamp requires a tension of 16 v. and a current of 0.25 amp. I have replaced the glass globe of the lamp by a tube made for the purpose which is shown in Fig. 1. A plate of fluorspar is hermetically cemented to the opening A, the tube B contains phosphorus anhydride and the filament is surrounded by a cylindrical tube of metal blackened on the

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#### No. 5.] ENERGY OF HEFNER STANDARD.

The lamp was supplied by current from eight large accumulator cells. The current was regulated by means of resistance in the circuit and was determined by means of an accurate ammeter. By means of a concave mirror of focal length 67 cm. an image of the source of light was projected upon the face of the bolometer. In Fig. 2 the following curves are shown : a, curve for the radiation of



the glow lamp with a current of 0.2 amp.; b, curve for the glow lamp with a current of 0.21 amp.; c, curve for the Hefner lamp.

From the beginning of the infra-red spectrum to about  $\lambda = 1.5 \mu$  the energy spectrum of the Hefner lamp is not affected by emission bands. In this region the spectrum corresponds very well with that of the glow lamp for a current of 0.21 amp., as will be seen from the following table in which are given the mean values of the intensity  $I_1$ , obtained by measuring three photographic plates of the spectrum of the glow lamp and of  $I_1$ , from five plates of the Hefner lamp.

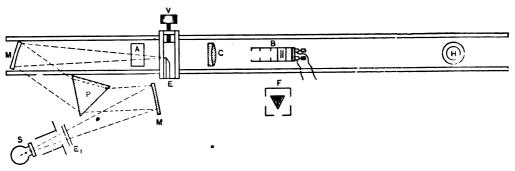
The spectral distribution being identical in the two cases,  $I/I_1$  should be a constant, and this will be seen to be the case from the numbers given in the fifth colum of the table.

Dev.	<b>X</b>	I	!	<i>I</i> 1	$\frac{1}{T_1}$
1°	0.90	6.9		7.9	0.875
1°5⁄	0.96	9.1		10.5	0.850
1°10⁄	1.06	12.2		14.5	0.844
1°15⁄	1.18	17.0	i	19.9	0.854
1°20⁄	1.33	22.8		27.5	0.830
1°25⁄	1.50	29.9		35.3	0.846

#### TABLE I.

III. DISTRIBUTION OF ENERGY IN THE VISIBLE SPECTRUM OF THE GLOW LAMP AND OF THE HEFNER LAMP.

To determine the distribution of energy in the visible spectrum I have employed the arrangement of apparatus shown in Fig. 3, in which MPM is a reflecting spectroscope with silvered mirrors. As a source of radiation I have used, the glow lamp described above.





The filament being very slender it was not necessary to furnish the spectroscope with a slit in order to obtain a sufficiently pure spectrum. By this apparatus a real image of the spectrum is produced of which a portion may be intercepted by a double screen E, movable perpendicularly to the bundle of rays by means of a micrometric screw V. The rays which pass the edge of the screen are concentrated at B in an image of uniform color by means of the cylindrical lens C. At B may be placed a bolometer or a photometer F. To avoid the disturbing influence of the radiation of heated portions of the instrument a water cell is placed at A. A screen  $E_1$  is used to cut off at will the radiation emitted by the

•

source S. All parts of the apparatus are mounted upon a very solid optical bench which permits of ready adjustment.

If E is withdrawn so that the whole of the visible spectrum passes it is evident that the image at B will be white. Placing at H a Hefner lamp and substituting a photometer F for the bolometer Bthe current in the glow lamp S may be so regulated that the light of this lamp at B will have the same color as that coming from the Hefner lamp. The current necessary was found to be 0.21 amp. and by spectrophotometric comparisons of the two lights under these conditions the distribution of energy in the spectra was found to be same; which agrees perfectly with the results already obtained in the infra-red spectrum.

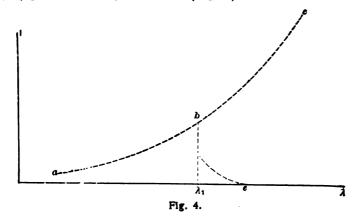
The photometer is now replaced by a spectroscope furnished with a scale the reading of which in wave-lengths has been determined experimentally. The screen E is advanced gradually and for each adjustment of the micrometer screw the limiting wave-length of the light which passes is determined. This done the spectroscope is replaced by a very sensitive bolometer and the radiation is determined for different positions of the screen E. In this way the total energy of that portion of the spectrum between the extreme ultra-violet is measured and a certain wave-length determined by the position of the screen ; that is to say  $\int_0^{\lambda} I_{\lambda} d\lambda$ . These values are designated by L and  $L_{\lambda}$ .

The radiation which passes the edge of the screen and which produces the effect upon the bolometer is evidently not altogether pure; it is mixed with stray light, that is to say with light that ought to have been intercepted with the screen. To correct the errors caused by this stray light I have proceeded as follows:

The spectroscope, furnished with a double Vierordt slit and with a rectangular diaphragm in the focal plane of the eye-piece, was mounted in such a position that the opening of the slit was at B, Fig. 3, so that half of this slit received the light from the glow lamp and the other half that from the Hefner lamp which served as a source of comparison. The intensity of the light in various parts of the spectrum, the screen E being completely withdrawn, was then determined; after which the intensity of the same regions

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was found for different positions of the screen. These measurements give the ratio between the stray light and the light in the original spectrum for various wave-lengths and positions of the screen. By introducing the values found for L as ordinates and wave-lengths as abscissæ, a curve is obtained by means of which one may, with sufficient exactitude for our purpose, construct geometrically the ordinary curve for the intensity I; for which purpose we make use of the fact that the tangent of the first curve  $(dL/d\lambda)$  gives I directly. Let abc (Fig. 4) be the curve thus found



and let the screen E intercept the spectrum at  $\lambda_1$ . By aid of the photometric determinations described above we can trace the curve representing the intensity of the stray light in the shaded region  $\lambda_1 \lambda$ . The ratio between the surface  $be\lambda_1$  and  $ab\lambda_1$  evidently gives the correction for the stray light; a correction which it is necessary to subtract from the original value of L. The correction was very insignificant, being for the following positions of the screen:

$$\lambda = 0.70 \,\mu \quad 1.2\%$$
  

$$\lambda = 0.65 \,\mu \quad 1.4\%$$
  

$$\lambda = 0.60 \,\mu \quad 1.4\%$$

## IV. DETERMINATION OF THE RADIATION OF THE HEFNER LAMP IN Absolute Measure.

To reduce the relative values to absolute measure I have first determined the total radiation Q of the Hefner lamp by means of my pyrheliometer with electric compensation<sup>1</sup> and then the ratio  $L_{0.76}/Q$  of the luminous radiation to the total radiation. I have thus obtained  $L_{0.76}$ ; after which it is easy to transform the other values of L into absolute measure.<sup>3</sup>

## (a) Determination of the Total Radiation.

The pyrheliometer employed in this experiment was a very good instrument with all the refinements due to experience. The strips for absorbing the heat were of manganin and of a width of 0.1497 cm., the resistance being 0.0915 ohms per cm. From these values I have been able to determine the constant of the instrument to be 0.1314 and I have computed the intensity of the radiation from the value of the electric current used in compensation by means of the equation

$$Q = ki^2 \frac{\text{gr. cal.}}{\text{sec. } \times \text{cm.}^2}$$

The current i was determined by means of an accurate amperemeter from Siemens and Halske. The equality of temperature of the two strips was indicated by a mirror galvanometer of great sensitiveness. The determinations have been made at two different distances from the lamp respectively 100 cm. and 50 cm. The results for a distance of 100 cm. are as follows :

From which we have

 $Q_{100} = 0.1314 (0.01275)^2 = 0.0000214 \frac{\text{gr. cal.}}{\text{sec. cm.}^2}$ 

For a distance of 50 cm. we obtain in the same way: Right side of pyrheliometer illuminated, i = 0.0253 amp. Left """"""" i = 0.0259"

<sup>1</sup> K. Ångström, Acta. Soc. Upsal., 1893; PHVS. REV., I., 365, 1893. <sup>2</sup> See my preliminary note : K. Ångström, Phys. Zeit., Vol. 3, 257, 1902. Whence

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$$Q_{50} = 0.1314 (0.0256)^2 = 0.000086 \frac{\text{gr. cal.}}{\text{sec. cm.}^2}$$

If from the latter determination we calculate the radiation for a distance of 100 cm. we get (evidently)

$$Q_{100} = 0.0000215 \frac{\text{gr. cal.}}{\text{sec. cm.}^2};$$

which is in good agreement with the preceding value. We have thus determined the total radiation corresponding to the *bougiemetre*.

(b) Determination of the Photogenic Efficiency L/Q.

For the determination of the ratio between the luminous radiation and the total radiation the arrangement which has been described above (Section II.) was used. The screen E was adjusted for  $\lambda = 0.76 \,\mu$  so as to intercept only the infra-red spectrum. The photometer F was placed at B and a Hefner lamp (see Fig. 3) was placed at H. The photometer (Fig. 3, F) consisted of a rectangular prism of chalk enclosed in a small black box with three circular openings, two of which were located face to face for the passage of the light to be examined, while the third was so placed as to enable the observation of the illumination of the two faces of the prism. The Hefner lamp was adjusted so that the light upon the two sides of the photometer was uniform. In this case the photometer receives on one side the total radiation from the Hefner lamp, on the other side only the luminous portion. By replacing the photometer with a sensitive bolometer for the purpose of measuring the intensity of these two bundles of rays, which are physiologically identical, we obtain the value L/Q.

I have obtained as the mean of four determinations on different occasions L/Q = 0.0096.

This determination is a very difficult one, the least variation in the adjustment of the screen causing large errors in the result. I

It is from this value of  $L_{0.76}$  that the values of  $L \times 10^8$  given in Tables II. and III. have been deduced.

# V. RADIATION IN THE LUMINOUS SPECTRUM OF THE HEFNER LAMP EXPRESSED AS A FUNCTION OF THE WAVE-LENGTH.

It may be taken as probable, *a priori*, that the spectral distribution of the energy of radiation both in the incandescent lamp and in the Hefner lamp may, by a suitable choice of constants, be expressed by means of formulæ given for the radiation of an absolutely black body. For the visible spectrum, where the wavelengths are relatively small, Planck's formula

(I) 
$$I = C_1 \lambda^{-5} (e^{c_y \lambda T} - I)^{-1}$$

and that of Wien

$$I = C_1 \lambda^{-5} e^{-c_2/\lambda T}$$

lead to the same result in practice. The latter being the more simple I have attempted to determine for it the constants  $C_1$  and  $c_2$  in such a manner that the formula shall represent the observations as well as possible. It is not however the intensity I which has been the object of our observations, but

(3) 
$$L_{\lambda} = \int_{0}^{\lambda} I_{\lambda} d\lambda = C_{1} \int_{0}^{\lambda} \lambda^{-5} e^{-c_{2}/\lambda T} d\lambda.$$

The temperature T being taken as constant in our sources of light, we may replace  $C_s$  by a constant c and obtain through integration the expression

(4) 
$$L_{\lambda} = C_1 \frac{e^{-c/\lambda}}{c^4} \left\{ \left(\frac{c}{\lambda}\right)^3 + 3\left(\frac{c}{\lambda}\right)^2 + 6\left(\frac{c}{\lambda}\right)^3 + 6 \right\}.$$

From the directly observed values of L, values have been obtained by interpolation of the means for  $\lambda = 0.50$ ,  $\lambda = 0.55$ ,  $\lambda = 0.60$ ,  $\lambda = 0.65$  and  $\lambda = 0.75$ . By the method of least squares I have deduced from these values the constants  $C_1$  and c by the aid of approximate values. This computation gives as a result, C = 0.0160, c = 7.85. The following table contains the observed values and the calculated values with their differences.

λ	$L \times$	( 10 <sup>8</sup>	_ Obs Calc.	/× 10 <sup>3</sup>
^	Obs.	Calc.		1 / 10
0.75	18.7	18.46	+0.24	19.26
0.70	10.4	10.67	-0.27	12.83
0.65	5.44	5.46	-0.02	7.85
0.60	2.61	2.51	-0.10	4.28
0.55	1.17	0.97	+0.20	2.02
0.50	0.34	0.30	+0.04	0.78

TABLE IV.

It will be seen that the difference between the computed and the observed values does not appear to pass the limits of the errors of observation. Consequently one may, with the degree of exactitude which the experiments permit, express the determination of the spectrum of the Hefner lamp by the formula

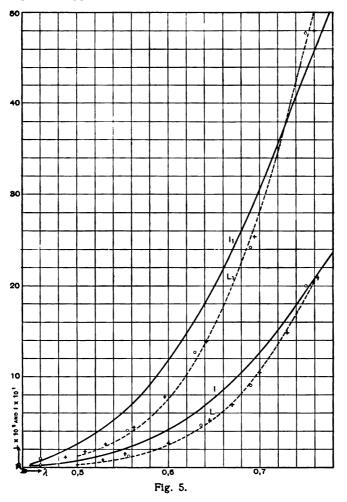
(5)  $I_{\lambda} = 0.0160\lambda^{-5}e^{-\frac{7.85}{\lambda}}$ .

The last column of the preceding table contains the values of I calculated according to this formula. The formulæ 4 and 5 are graphically represented in Fig. 5, the former by means of the curve marked I, the latter by means of that marked L. The first gives directly the energy between two wave-lengths  $\lambda_1$  and  $\lambda_2$  by means of the differences between the corresponding ordinates. The curve I is an ordinary curve for intensities.

Paschen and Wanner<sup>1</sup> have determined the constant  $c_2$  in formula 2 for the radiation of a black body and have found  $C_2 = 14,440$ . Since in formula (5) we have  $c = 7.85 = C_2/T$ , we may determine the absolute temperature of a black body emitting radiation equal to that of the Hefner lamp. We obtain for this the value  $T = 1,830^\circ$ .

This value is in good agreement with the determination of Lummer and Pringsheim<sup>2</sup> who by use of Paschen's law,

have determined T for various sources of radiation under the supposition that the constants are comprised between 2.940 and 2.630, values determined respectively for the radiation from a black body and from platinum. For a candle, the conditions of radiation of which appear to approach most nearly that of the Hefner lamp, they



have obtained  $T_{\text{max.}} = 1.960^{\circ} T_{\text{min.}} = 1.750^{\circ}$ . I also sought to determine the constant c for the incandescent lamp when the current in the circuit was 0.253 amp. I found c = 7.24 (taking  $C_2 = 0.0160$  as in the previous calculation). The corresponding curves  $L_1$  and  $I_1$ 

are also represented in Fig. 5 with the observed values so that it is possible to compare the observed and calculated values. The temperature in this case corresponds to  $2,000^{\circ}$ .

Our investigations show that Wien's law represents very well the distribution of energy in the luminous spectrum of the Hefner lamp and of the incandescent lamp. After having thus determined in absolute measure the radiation and the constants for the Hefner lamp in Wien's formula, it is easy to measure photometrically the energy of radiation and its distribution in the visible spectrum of any radiant source whatever, with an exactitude sufficient for many purposes. It is only necessary to compare the source of light in question and the Hefner lamp for a certain part of the spectrum lying between  $\lambda_1$  and  $\lambda_2$ . The curve *L*, Fig. 5, then enables us to find readily the energy in that portion of the spectrum by taking the difference between the corresponding ordinates.

It is obvious that the present researches have been of a preliminary nature. It is evident, for example, that the bands, which in the visible spectrum of the Hefner lamp are doubtless superimposed upon the continuous spectrum, produce deviations, small perhaps, from the law of radiation of a black body. I hope nevertheless that these results will have a certain importance in the study of feeble sources of light, of certain phenomena of luminescence and even in physiological optics.



## NEW BOOKS.

Principles of Inorganic Chemistry. By HARRY C. JONES. New York, The Macmillan Company, 1903. Pp. xx + 521.

"The aim of this book is to add to the older generalizations those recently discovered, and to apply them to the phenomena of inorganic chemistry in such a way that they may form an integral part of the subject, and, at the same time, be intelligible to the student. Why should we continue to teach the chemistry of atoms to students on the ground of its being a little simpler, perhaps, than the chemistry of ions, or on any other ground if we know that it is not in accordance with the recently discovered facts? Or why should we continue to teach purely descriptive chemistry when the science of chemistry has outgrown this stage, and many of the most important relations have been accurately formulated in terms of the simpler mathematics?"

This quotation from the author's preface gives the key to his treatment of his subject. He has written a book on inorganic chemistry which is almost physical chemistry with its illustrations all chosen from the inorganic field. More than this, the book is written from the standpoint of the theory of electrolytic dissociation, whereas the phase rule, the law of mass action and other important generalizations are lightly treated. The author leaves us in no doubt about his devotion to the dissociation theory when he says in this preface, "We know to-day that nearly all inorganic reactions are reactions between ions; molecules and atoms as such having nothing to do with the reactions." He treats the whole subject furthermore as if these physical chemical generalizations were complete and final.

That these newer generalizations are valuable as aids in explaining many otherwise puzzling phenomena is generally admitted. But they may easily be overworked, and in the case of this book one has the feeling that the ionization theory has been. It is doubtful if Dr. Jones' book will fulfill its aim of being intelligible as far as the elementary student is concerned, and if it is intelligible to him the student will have an erroneous idea of the relation between the newer and the older generalizations.

The elements are grouped for study generally as they are in the Periodic Table, after the three elements, oxygen, hydrogen, chlorine more or less typical, as the author calls them — have been taken up in some detail. The arrangement is generally good, though it is difficult to see just why neodymium and praseodymium should be considered with vanadium, columbium, and tantalum, and not with lanthanum and the yttrium group. Among other omissions the author fails to give double salts more than very slight mention.

The book is well gotten up and the type is good, but the proof-reading was poor and the trivial errors are many.

Errors of fact like the following should not have crept into a text on inorganic chemistry. It is stated on page 254 that phosphorus oxychloride is formed by the action of water on the trichloride or on the pentachloride of phosphorus. This is not true as regards the action of water on trichloride. On page 305 we are told that bauxite is a titanium mineral, and on page 407 that it is a hydroxide of aluminum and iron; iron is nearly always, perhaps always, present, but bauxite is essentially a hydrated oxide of aluminum. On page 306 we are told that "thorium usually acts as a trivalent element forming salts of the type ThCl<sub>a</sub>, Th<sub>a</sub>(SO<sub>4</sub>)<sub>a</sub>, etc."; it is tetravalent in its salts. On page 315 sodium hydride is given the formula NaH, and on page 335 that for potassium hydride is similarly given KH. On page 334 metallic potassium is said to set metals such as aluminum free from their oxides; this is at least not true in the case of aluminum (see Goldschmidt and Vantin, J. Soc. Chem. Ind. 17, 543). And why should the student be left with the impression that the "D" line is single, as is done on page 332; or that a single bright green line constitutes the barium spectrum, as on page 381? The melting point of rubidium is 38.5°, not 158°, as given on page 354.

The work is interesting reading to the advanced student, as it brings forcibly before him the general relations of the facts with which he is familiar. BENTON DALES.

An Elementary Treatise on the Mechanics of Machinery. By JOSEPH N. LE CONTE. New York, The Macmillan Company, 1902. Pp. 303.

Professor Le Conte has divided his subject into three parts: (1) An introduction, in which the general principles of kinematics are briefly demonstrated; (2) machinery of transmission; (3) the mechanics of the steam-engine, including both kinematics and dynamics.

To treat so broad a field within the compass of 300 small octavo pages results in a certain lack of proportion — which is the most serious fault to be found with the book. The author's trend of mind is toward rigid analytical demonstrations, leading him at times to apportion his available space in accordance with the mathematical difficulties of his topics rather than their importance in practice. However, when the result is so satisfactory as his treatment of skew wheels, for instance, one feels inclined to withdraw any objection. Guido H. MARX. No. 5.]

Vorlesungen ueber Experimentalphysik. By August Kundt, edited

by KARL SCHEEL. Pp. xxiv + 852. Braunschweig, Vieweg, 1903. The lectures on experimental physics delivered by the late Professor Kundt during the last five years of his life, 1889-1894, in the Physical Lecture Room of the University of Berlin, will be remembered with great pleasure by all those who were fortunate enough hear them, on account of the unusual wealth and originality of the illustrations presented and of the clearness and simplicity of statement with which the demonstrations were accompanied. In the present volume these lectures, essentially in the original form of the manuscript notes of the author, are given to the public. The decision to retain as nearly as possible the condition and arrangement of the manuscript, making only such changes as were necessary to prepare the same for the press, was a wise one. We have as a result of this conservatism on the part of the editor a faithful record of the beginner's course in physics as it was given in the University of Berlin fourteen years ago; instructive from the standpoint of the development of the science, no less on account of what it does not than of what it does contain. The treatise comprises a year's work, eighty-seven lectures in the winter semester on mechanics, sound and heat and sixty-three in the summer semester on electricity and magnetism and light. There are neither footnotes nor references to the original sources. E. L. N.

## Alternate Current Transformer. By F. G. BAUM. Pp. i + 188. New York, McGraw Publishing Company, 1903.

After a brief outline of elementary principles, the writer discusses the graphical representation of pressure relations. As a basis, the secondary electromotive force is considered as being due to changing magnetism, rather than as due to changing primary current. The reviewer agrees with the writer that this treatment is to be preferred, since it more nearly represents the physical facts. The following four chapters, on regulation, efficiency, testing and design, constitute the useful portion of the book. The treatment in these chapters is good, being brief and to the point. The last third of the book, while containing some good material on transformer connections, is somewhat dilute, being interspersed with trade cuts of commercial types and descriptions of special appliances.

On the whole the book should form a satisfactory student manual; the treatment is sound and for the most part clear. The parts are well balanced and the author's individuality is shown throughout. The book is far from "mechanically as perfect as possible" as indicated in the preface.

Modern Chemistry. By WILLIAM RAMSAY. Part I., Theoretical Chemistry, 120 pp. Part II., Systematic Chemistry, 203 pp. The Temple Cyclopædic Primers. London, J. M. Dent and Company; New York, The Macmillan Company.

These little volumes present in brief and compact form the chief facts and theories of modern chemistry. The theoretical part is not a text-book on physical chemistry but the subject is presented from a physico-chemical standpoint with a breadth of view and a due observance of relative proportions that are admirable. In Part II. the same classification is followed as was used in the author's text-book, "A System of Inorganic Chemistry." The hydrides of all the elements are first considered, then the halides, the oxides and hydroxides, etc. This presents the subject from a point of view that differs from the customary one and that has many advantages. The style is clear, the books are eminently readable, and the amount of matter that Professor Ramsay has succeeded in compressing into their small compass is surprising.

THEODORE WHITTELSEY.

Lehrbuch der Kosmischen Physik. Von S. ARRHENIUS. Pp. viii + 1026. Leipzig, S. Hirzel, 1903.

In this treatise the term *cosmic physics* is taken in the broader sense of the word. It includes astrophysics and the physics of the earth's crust, to which two subjects, Part I. (containing 472 pages) is devoted, and meteorology, or the physics of the atmosphere, to which the remainder of the volume is given. The point of view and method of treatment throughout are those of the physicist rather than of the astronomer, the geologist or the meteorologist respectively.

As a work of reference Professor Arrhenius' treatise will be found of special value to the student of physics. It contains a wealth of interesting and important material which is excluded from the ordinary text-books and manuals of experimental physics for lack of space and which is omitted in the corresponding works on astronomy, geology and meteorology for the very reason that it is frequently of interest to the physicist rather than to the student of those sciences. E. L. N.

Lehrbuch der Physik. Von O. D. CHWOLSON. Erster Band. Übersetzt von T. H. PFLAUM. Pp. xx + 791. Braunschweig, Vieweg, 1902.

This German translation of Chwolson's compendious treatise renders a very valuable book available to a larger public. In bringing it out in its present form the translators and publishers are doing more than to

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NEW BOOKS.

nature of physical theories, hypotheses, laws and quantities is discussed. This is followed by a section devoted to mechanics; and under this head the author deals with motion, force and energy. Harmonic motion and wave systems are treated at considerable length and a number of topics are dealt with in this portion of the work which are frequently deferred until the subject of optics is reached. We find in this section on mechanics, for example, Huyghen's principle, the laws of diffraction, reflection and refraction and the principle of Doppler; from which the author returns to the consideration of universal gravitation, the potential theory and the pendulum. This section closes with a chapter on the dimensions of physical quantities.

One meets occasionally in this portion of the work conceptions of doubtful utility; as for example on page 89 where the gram is spoken of as a unit of force and equal to 981 dynes. On page 96 we find the field of force defined as a medium which possesses properties such that upon a body at a given place within the same a force acts which is proportional to the mass of the body.

The section upon mechanics is followed by one descriptive of instruments and methods of measurement and this contains a series of very useful chapters on dividing engines, and micrometers of various types; on planimeters and instruments for the measurement of angles; on the measurement of volume, of mass, and of the force of gravitation. The volume closes with a discussion of the properties of gases, liquids and solids, taken in the logical, but unusual, order given above.

References to the literature are gathered at the end of each chapter instead of being introduced in the form of footnotes and the citations are arranged in the order in which the various topics are taken up in the text. The usefulness of the treatise as a work of reference is further enhanced by an author's index and a fairly complete index of subjects.

Aside from its merits as a treatise on general physics, in which respect Professor Chwolson's work may be ranked with the standard manuals of the German authors, this work will have the advantage of bringing to the great body of working physicists to whom Russian is a closed book, a more complete knowledge of the contributions of Russia to our science. In addition to the memoirs and bulletins of the Academy of Sciences at St. Petersburg, frequent reference will be found to the journals of the Russian Physical Society, and the Moscow Association of Naturalists and to the programmes and publications of the various Russian universities.

E. L. N.

print that the present new edition will be gladly welcomed. No additions or changes have been made; the edition is in fact a facsimile reprint of that of the year 1870. The editor's preface, in addition to a very brief account of the life of Green, gives a short sketch of each of his papers. The best known of these and the most important is probably the first — "An Essay on the Application of Mathematical Analysis to the Theories of Electricity and Magnetism." It will be remembered that this paper was originally published by subscription in 1828, before its author had begun his studies as an undergraduate at Cambridge. In it the term *potential* was first introduced and many of the properties of the potential function were investigated for the first time. In this paper also the celebrated "Green's Theorem" was first stated and proved, while its numerous applications in the theory of electricity were well illustrated.

The volume contains in all eleven papers. Among the other papers that have been of special importance in the development of Mathematical Physics, the following may be mentioned: The Determination of the Exterior and Interior Attractions of Ellipsoids of Variable Densities; The Motion of Waves in a Variable Canal of Small Depth and Width; The Laws of Reflection and Refraction of Light at the Common Surface of Two Non-Crystallized Media; On the Propagation of Light in Crystallized Media. E. M.

# Handbook of Climatology. By JULIUS HANN. Translated by R. DEC. WARD. New York, The Macmillan Co., 1903. Pp. 429.

Hann's Handbuch der Klimatologie has long been a standard on the subject, but the fact of its being in German has prevented its use in America excepting by certain specialists. In order to make the book of use to students at Harvard University and elsewhere, Professor Ward has translated the first volume of the second edition. While the book is in the main a translation of Hann's original publication, Ward has added a number of new points from the standpoint of American climatology and both the translation and the insertions have received the approval of Dr. Hann.

The Centigrade scale and metric system are used in the volume, but at the end are a series of conversion tables. Professor Ward is to be commended for the sacrifice which he has made in rendering this valu-

# THE

# PHYSICAL REVIEW.

# THE LUMINOUS EFFICIENCY OF VACUUM-TUBE RADIATION.

#### BY E. R. DREW.

"HE radiation which is produced when an electric current is passed through a rarefied gas has a special interest on account of the comparatively small increase in temperature which accompanies it. The early investigators seem to have assumed that the temperature in the vacuum-tube discharge is of the same order as that in luminous flames. Hittorf among others doubted this, and adduced several considerations<sup>1</sup> which tended to show that it must be much lower. E. Wiedemann<sup>2</sup> immersed the capillary portion of a vacuum-tube in a calorimeter, and measured the heat developed by each discharge of an induction coil through it. Apparently assuming that the heat developed first raised the temperature of the gas before any appreciable conduction took place through the glass walls of the tube, he calculated the rise in temperature from the specific heat of the gas. His results are of the order of 80,000° for the capillary, which is doubtless too high ; but he concluded that in the wider part of the tube there might be considerable light radiation with a temperature below 100°.

The portion of a vacuum tube immediately surrounding the anode, and that surrounding and, at lower pressures, extending some distance from the cathode, does not lend itself readily to such investigations, because of the lack of uniformity in the electrical conditions. For this reason the so-called "positive column," which extends

> <sup>1</sup> Wied. Ann., 7, 575, 1879. <sup>2</sup> Wied. Ann., 6, 298, 1879

from just in front of the anode some distance toward the cathode, where these conditions approach much more nearly to uniformity, has been the usual subject of study. Warburg<sup>1</sup> calculated the temperature in this region for several cases, on the assumption that the electrical energy which disappears is all converted into heat; this being measured by the product of potential gradient and current strength. The results thus obtained agree quite well with the values later found by Wood,<sup>2</sup> who measured the temperature directly by means of a bolometer wire inserted in the tube across the path of the discharge. The temperatures thus found are often only a few degrees above that of the surrounding air.

K. Ångström was one of those who recognized the fact that the radiation from a vacuum-tube must be of a different character in some respects from that which comes from incandescent gases and One of the characteristics of the latter class, which radiate solids. on account of their high temperature, is that the radiation covers the whole range of frequencies up to the highest which is present, this latter, and also the proportion of high-frequency radiation to the total, increasing in general with the temperature. Ångström<sup>3</sup> measured the total radiation from a vacuum-tube, by means of a bolometer, and also the portion which is transmitted by a plate of alum, under different conditions. The ratio of this portion to the total may for convenience be called the luminous efficiency, although it is well known that the radiation transmitted by the alum plate extends somewhat beyond the red end of the visible spectrum. He found that this ratio is quite different in different gases, while for the same gas it increases continuously as the pressure decreases, and at a given pressure is apparently independent of the current. The chief point of interest, however, is the fact that the efficiency is much higher than is the case with sources of light which radiate on account of their high temperature. In the case of nitrogen at a pressure of 0.15 mm. it reaches a value above ninety per cent.

found them to be in agreement with the corresponding results which Ångström had found for the total radiation.

These results make it highly probable, as Angström and others have pointed out, that when radiation is emitted by a gas, in one case by heating it, and in another case by sending a current through it, the mechanism which is brought into play must differ in some important respects in the two cases. It was in the hope of gaining some further knowledge in regard to this mechanism that the present investigation was begun, along the same general lines as that of Angström. After giving an account of the experimental methods and results, an attempt will be made to account for the latter, so far as possible, in terms of the modern electron theory, which has proved so useful in its application to the varied phenomena which attend the passage of electricity through gases.

## EXPERIMENTAL.

Radiometer. - A radiometer was used for measuring the radiation from the tube; partly because the magnetic disturbances about the physical laboratory make it troublesome to work with the sensitive galvanometer which would be required for a bolometer or thermopile, and partly because it has some inherent advantages over the latter. It is less trouble to construct and use at a high degree of sensitiveness, and its lack of mobility is no objection for the present purpose. The instrument as constructed happens to correspond quite accurately, in its essential features, with the one which E. F. Nichols<sup>1</sup> used in his determination of the radiation from stars and planets. The suspended system is larger, the mica vanes being 3 mm. in diameter instead of 2, and 7 mm. between centers. It weighs about 12 mg. The window through which radiation enters at f, Fig. 3, is of fluorite, very clear and about 1 mm. thick. The vanes are about 2 mm. behind this window, at v. A small glass window g, behind the vanes, through which they can be seen, is set at an angle, so that radiation entering through the window in front and passing the edge of the vane will not be directly reflected upon its rear face, but will fall instead upon the blackened interior walls of the case. When the necessary screens were put in front of the fluo-

<sup>1</sup>Astrophys. Jour., 13, 101, 1901.

rite window, as will be described later, and the whole instrument, except the window apertures, surrounded by a thick layer of wool, there was very little trouble from zero drift due to the ordinary temperature changes in the room.

The relation between sensitiveness and pressure seems to vary considerably in different instruments. In the one described by E. F. Nichols the sensitiveness is a maximum at about 0.05 mm. pressure, and the curve is rather flat at that point; while one used by G. W. Stewart,<sup>1</sup> which seems to be of similar construction, shows a quite sharp maximum at about 0.10 mm. The corresponding curve for this instrument (Fig. 1) may, therefore, be not without in-

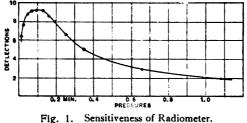


Fig. 1. Sensitiveness of Radiometer.

terest. The sensitiveness changes very little through the range of pressures from 0.04 mm. to 0.15 mm., which was quite convenient, as it proved impossible to prevent a slight leak. At pressures below 0.1 mm., the period is approximately forty-five seconds. At higher pressures, the swing is aperiodic, the full deflection being approximately reached in a time which increases slowly from fortyfive seconds with the pressure.

The maximum sensitiveness is such that a paraffin candle burning normally at a distance of 200 cm. causes a deflection of about 30 cm. on a scale at a distance of 100 cm. This is about one half as great as that given by Nichols for the first instrument which he constructed, and about twice as great as for the one mentioned above.

Some of the readings with the vacuum-tube seemed to indicate that the larger deflections were not proportional to the energy, and a calibration of the scale showed this to be true. A 105-volt 16-

that the radiometer was affected only by radiation which came from the lamp directly, and not by reflection. The results, plotted in Fig. 2, show that a deflection of 20 cm., which is the largest used, is about 12 per cent. too small. This large deviation is due doubtless to the fact that the vanes are so near the window, and especially that the one which is screened from radiation has a part of its surface opposed to the brass flange on the inside of the window, at a still less distance.

Vacuum-Tube. — Ångström used several tubes in his work, but they were all of nearly the same diameter. He suggested that it

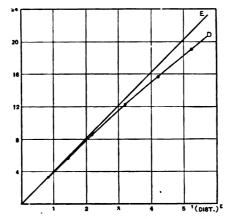


Fig. 2. Calibration of Radiometer. E, energy; D, deflection.

would be interesting to find the efficiency for tubes of widely differing diameters, and this was chosen as the first point of attack. The form of the tube, and the arrangement of tube, radiometer and screens, is shown in Fig. 3. The board to which the tube is secured is pivoted to a support at A, the intersection of the axes of the two branches, so that by swinging vertically about this pivot the axis of either branch may be brought into the horizontal line through the center of the radiometer vane. The smaller branch has an internal diameter of 9 mm., the larger of approximately 18 mm., and the length of the luminous column in each is about 10 cm. The aluminium electrodes in the side tubes are cylindrical, giving large surface, so that the heating is small. The ends of the two branches next the radiometer are closed by fluorite windows 1 mm. thick. These, as well as all of the radiometer windows, are fastened with de Khotinsky cement.

A copper screen with a circular opening 4 mm. in diameter, I mm. larger than the vane, is placed about 3 cm. in front of the vane at a. Outside the radiometer case, about 5 cm. from the vane, is a larger double screen with a slightly larger opening. These serve to cut off from the vane all radiation except that which comes from the tube, and even with the smaller tube, a considerable share of the secondary radiation which may come from the heated tube walls. Between the end of the tube and the double screen space is left for the insertion of a cell w, which contains a layer of water I cm. thick between glass walls I mm. thick. Although this transmits more than the visible radiation, as did the alum plate used by Ångström, it still gives a definite division of the total radiation, which is sufficient for the immediate purpose in hand.

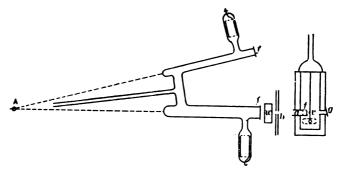


Fig. 3. Vacuum Tube and Radiometer.

Pressure Gauge, Pump and Connections. — For reading pressures a McLeod gauge was constructed in which the small tube is about 4 mm. in diameter, and the capacity of bulb 80 c.c. This enables pressures from 2 cm. to 0.01 mm. to be read with the necessary accuracy, and gives results which are consistent to within the error of reading, as well as can be judged by taking readings for the same pressure with different degrees of compression in the small tube.

Reduced pressure is obtained by means of a Geryk oil pump, with which pressures down to 0.01 mm. can be obtained easily and rapidly.

The gauge and pump, with the usual drying-tube containing phosphorus pentoxide, is connected to the vacuum-tube by a short VACUUM TUBE RADIATION.

piece of rubber tubing, which is necessary to allow the required rotation of the latter, and by a longer piece to the radiometer, which can be closed from the rest of the apparatus by a glass stopcock. This rubber tubing, and the numerous joints, made it impossible to prevent leakage entirely. As air was the only gas used, and the leakage was small, it caused little trouble.

## EXPERIMENTAL DETAILS.

Alternating Current. — A large amount of preliminary work was done with an alternating current, chiefly on account of the ease with which it could be obtained. A city lighting circuit of 55 volts, 120 alternations per second, was connected through a rheostat to the primary of a large Charpentier induction coil, and the secondary connected to the terminals of the tube. It subsequently proved that the ratio of transformation of the coil was by no means constant, but varied with the resistance in the secondary circuit in a way which tended to keep the current constant.

Others who have used the radiometer have been troubled by electrification of the vanes, which usually occurs during the exhaustion, and persists for some time. When symptoms of this trouble appeared in the use of the present instrument, it was thought that the discharging action of radium might be utilized here by putting a few grains inside the radiometer. The result was a new and puzzling complication. There was still evidence of the usual electrification during exhaustion, which however quickly disappeared; but when a current was passed through the tube, there resulted what appeared to be an electrification effect, shown by a large shift of the zero, sometimes in one direction and sometimes in the other, which would disappear only after fifteen minutes or more. This made it impossible to determine the effect due to radiation alone. After some time spent in an attempt to discover the nature of the difficulty, and find a remedy for it, the radium was cleaned out as thoroughly as possible, and the effect soon became so small as to cause little trouble.

One of the difficulties experienced by Ångström was that due to radiation from the heated walls of the vacuum-tube, which sometimes contributed a large share to the effect on the bolometer. It was reasonable to expect that this effect would prove troublesome with

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the smaller tube at least. It was tested several times with various currents and pressures, by screening the radiometer from the tube while the current passed for the usual time necessary to read a deflection, then removing the screen immediately after stopping the current and noting the deflection. This rarely amounted to more than one per cent. of the deflection which would have been produced by the current had the screen not been interposed. When the radiometer was exposed during the passage of the current the effect seemed to be somewhat greater, as nearly as could be judged by the time taken to return to zero with and without the water-cell interposed. The method of reading finally adopted to diminish these errors as far as possible is to pass current through the tube during 45 seconds, which usually gives a little less than the full deflection, then read the zero one minute after stopping the current. No shutter is used, as it would usually be at a temperature different from that of the tube, which is in the radiometer field during an exposure.

The first determinations of the efficiency ratio showed that it varied with the pressure in the way which would be expected, and that it was notably higher in the smaller tube. These results will not be quoted, as much more trustworthy ones were obtained later.

Besides the city circuit, there was available a University lighting circuit of 1,000 volts, 240 alternations per second. This was applied directly to the terminals of the tube, through a rheostat of cadmium iodide in amyl alcohol, and also transformed down to 50 volts, then transformed up again by the induction coil. The discharge through the tube differed greatly in appearance with these three kinds of current, and it seemed worth while to determine whether the efficiency would show corresponding variations.

- a denotes city circuit, 55 volts, through induction coil.
- b denotes 1,000 volts transformed down to 50, then through coil.
- c denotes 1,000 volts on tube direct.

When the discharge through the small tube was viewed in a rotating mirror, or photographed on a falling plate, with (a) the band of light was almost continuous, a narrow dark space marking the interval, showing that the discharge occupied a smaller fraction of the total time. With (c), the available potential difference at the electrodes of the tube was less, and the discharge would only pass at pressures less than I mm. The discharge now occurred at the crest of the e.m.f. wave, and occupied not more than one third the total time.

Several sets of determinations of the efficiency ratio failed to show any definite difference for these three cases. One set of such results is given below. Each result quoted is the mean of two determinations, for which the order of reading radiometer deflection, with and without the water-cell interposed, is reversed.

 
 TABLE I.

 Efficiency with different kinds of alternating current. Small tube. Pressure of air between 0.4 mm. and 0.5 mm.

· · · · ·		
a	ь	c
.508	.480	.497
.502	.501	.521
.507	.492	.509
.511	.524	.519
.509	.529	.527
.513	.498	.512
.509	.485	.509
Mean .508	.501	.513

The slight differences among the mean results are hardly greater than the probable error.

An attempt to measure the current through the tube proved so unsatisfactory that it is worthy of description. A Weston alternating current voltmeter reading to 600 volts, resistance 21,600 ohms, was the only instrument at hand which would give readable deflections when used as an ammeter in series with the tube. In this type of instrument the lower part of the scale is much contracted, and the error of reading may be as great as five per cent. The deflections showed no evidences of electrostatic disturbances. For the three kinds of current, readings were taken of the current as given by the ammeter, and of the radiometer deflection for the total radiation from the tube. A preliminary trial showed that these are approximately proportional for one kind of current; and as it was not always convenient to obtain the same current, this proportionality was used to reduce radiometer deflections to the same ammeter reading.

The effect of the current in producing radiation in the tube is thus not at all proportional to the electrodynamometer effect as shown by the voltmeter. The appearance of the discharge when viewed in a rotating mirror indicates that the wave-form may be quite different in the three cases. The voltmeter may not read cor-

Τa	BLE	I	I.

Radiometer and ammeter effects of current. Pressure 0.4 mm.

Ammeter Current.		Radiometer Deflection,	Deflection Reduced to Current 0.008.	
a	0.0062 amp.	11.3 cm.	14.6 cm.	
ь	0.0081	12.5	12.4	
C	0.0079	8.8	8.9	

rectly for currents in which the wave differs greatly from the simple sine form; and it is to be noted also that the radiometer effect is proportional to the mean first power of the current, and the voltmeter reading to the square root of the mean square.

Direct Current. — The subsequent work was done with a direct current chiefly, in part because of these difficulties in measuring the alternating current, and also because any considerations based on the electron theory would require a knowledge of the potential gradient in the tube at the time of taking the radiometer readings. The potential gradient would have no very definite meaning in the case of the alternating current, nor could it be readily measured.

The available source of direct current is a battery of twenty-four small Crocker-Wheeler dynamos, each giving 500 volts, connected in series. Eight of these were ordinarily used, giving about 4,000 volts, which is sufficient to send the discharge through the tube at pressures up to about 5 mm. The current is read by a Weston standard milli-voltmeter, resistance 9.06 ohms, used as an ammeter, on which a current of 0.001 ampere gives a deflection of 4.5 scale-

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electrostatic disturbances, which without this precaution would often cause the needle to stick. In the cadmium iodide rheostat which is included in the circuit the upper electrode is suspended in the tube by a cord, so that its height can be readily varied as necessary in order to keep the current at the desired value. There are small irregular changes due probably to variation in the speed of the dynamos, and also an increase in current for a few seconds on first starting current through the tube, which may be due to something in the nature of a resistance which decreases with rise of temperature, since it is proportionally larger with larger currents.

The two deflections of the radiometer, with and without the water-cell, from which an efficiency ratio is calculated, must correspond to the same total radiation, so this adjustment to keep the current constant is quite important. The fluctuations can usually be kept within one per cent. The sensitiveness of the radiometer does not change appreciably during the short time covered by the two readings, nor does the pressure in the tube, except at very low pressures, as will be mentioned later.

The usual telephone method for testing the steadiness of the current through the tube was not very satisfactory, as there is always a faint hum in the telephone caused by the minute fluctuations in e.m.f. at the commutators on the dynamos. There was no fluctua tion other than this, so far as could be judged by comparison with the effect produced when the current flowed through the rheostat only, without the tube. The resistance outside the tube was never greater than  $8 \times 10^5$  ohms; and Hittorf<sup>1</sup> found no evidence of unsteadiness in the discharge, under similar conditions, until the outside resistance reached  $3.5 \times 10^6$  ohms.

Efficiency — Variation with Pressure, and with Tube Diameter.— The series of observations for finding the efficiency as a function of the pressure, in the two tubes separately, is given in Table III. The observed radiometer deflections, after correction from the calibration curve, Fig. 2, are tabulated in the order in which they were taken. The same current-strength was used throughout. Series I. and II. were taken on different days. In series III. are collected a number of single determinations which were made, under comparable con-

<sup>1</sup>Wied. Ann., 7, 563, 1879.

## E. R. DREW.

# TABLE III.

Variation of Efficiency with Pressure. a, Corrected Radiometer Deflection for Total Radiation. b, Corrected Radiometer Deflection for Water-Cell Radiation. e = b|a, Efficiency Ratio. p, Pressure in Millimeters. Current, 0.007 Amperes.

		Small Tube	.—Series I.			
a	т в — — — — — — — — — — — — — — — — — —	a		Mean, e	*	
	4.77	20.40	.234			
19.92	4.80		.241	.237	4.3	
	5.48	19.07	.288			
18.87	5.37	· ·	.285	.286	3.3	
	5.75	18.16	:317			
17.60	5.65	1.	.321	,		
	5.56	17.50	.318	.319	2.6	
	5.41	17.41	.311	;		
17.00	5.44		.320	.315	2.7	
	6.08	16.92	.360			
16.56	5.94	1	.359	1		
	5.94	16.56	.359	.359	2.14	
16.86	5.90		.350	2		
	5.71	16.43	.348			
16.50	5.88	•	.351	.350	1.9	
	6.52	17.31	.376			
16.70	6.38	1	.382	.379	1.52	
16.58	6.42		.388		88	
	6.21	16.36	.380	.384	1.25	
17.11	6.88		.402	.397		
	6.74	17.15	.393		1.0	
	9.01	19.90	.453			
20.55	9.05	, ,	.441	.447	0.66	
	<sup>°</sup> 8.94	18.98	.471	1		
18.67	9.07	1	.486	.478	0.46	
		Serie	= II.			
22.75	9.25	1	.408			
	8.87	22.26	.399	.403	1.12	
23.00	9.75		.425			
	9.58	23.30	.412	.418	0.85	
20.37	10.00		.492			
	9.88	20.61	.480	.486	0.40	
		Serie	s III.			
	mean	of 7		.262	3.85	
11.83	3.87		.327			
	3.82	11.92	.320	.323	2.95	
6.46	2.00	1	.310			
6.38	1.99		.312			
	1.97	6.40	.308	.310	2.95	

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### TABLE III.—Continued. ----

-		Large Tub	eSeries I.			
				Mean, c		
	-		-	MORI, C	_ /	
	0.66	9.56	.069	-		
8.97	0.54		.060	.064	4.3	
8.65	0.51		.05 <b>9</b>	1		
	0.53	8.00	.066	.062	4.4	
	0.56	5.90	.095			
5.66	0.59		.104	t į	3.3	
5.62	0.57		.101	.100	4.4	
4.50	0.57		. 127			
	0.56	4.27	.132	1		
4.32	0.55		. 127	.129	2.7	
3.06	0.41		.134	1		
	0.43	3.19	.135	.135	2.36	
3.04	0.46	I	.152	1		
	0.46	2.96	.156	.154	1.84	
	0.52	2.48	.210	1		
2.38	0.49		.206	.208	1.56	
	0.56	2.28	.245	1		
2.16	0.56		.259	.252	1.23	
1.94	0.60		.309	1		
	0.60	1.98	.303	.306	1.02	
2.02	0.68		.336			
	0.66	2.01	.328	.332	0.66	
	1.31	2.79	.470	1		
2.87	1.28	(	.446	.458	0.46	
		Seri	es II.			
	0.43	1.69	.255	1 1		
1.73	0.41	1.07	.235	.246	1.23	
3.08	0.81		.263	.263	1.10	
2.68	0.82	1	.306	.203	1.10	
2.00	0.78	2.60	.300	.303	0.85	
2.76	0.92	2.00	.334		0.05	
	0.92	2.75	.316	.325	0.68	
3.16	1.21	<i>4.13</i>	.310	.343	0.00	
	1.19	3.22	.382	.376	0.52	
				.370	0.32	
4.05	0.40		.099	·		
	0.40	3.58	.113	1		
3.69	0.38	5.50	.103	.105	3.1	
5.09 6.81	0.38	4	.103	.105	3.1	
	0.80	6.70	.120			
6.62	0.87	0.70	.130	.130	2.6	
· · · · · · ·	0.07		.134	.130	2.0	

ditions, during later work. The current was always sent through the tube so that the branch used was next the anode. Usually observations were made on the two branches alternately, to insure similarity of conditions.

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Immediately after Series I. and II., a similar set of readings was taken with the alternating current from the city circuit. It was assumed that the radiometer sensitiveness had not changed appreciably, and the radiometer effect was taken as an appropriate measure of the current. At each pressure then the current was adjusted, by means of the rheostat in series with the primary of the induction-coil, until the radiometer deflection for the total radiation was nearly the same as had been observed with the direct current. The

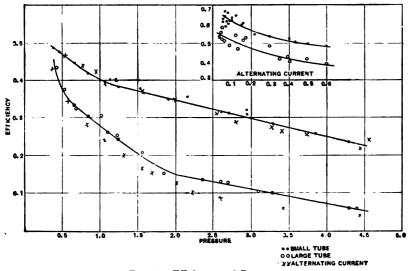


Fig. 4. Efficiency and Pressure.

measurements were otherwise carried through in precisely the same way as with the direct current.

Fig. 4 shows the direct current results graphically; and the alternating current results are added for comparison.

The direct current gives a continuous luminous column filling both branches of the tube at the higher pressures. When the sharply defined, and remain to the lowest pressures used. When the anode is next to the large branch, striation begins there at about 1.6 mm., and becomes gradually more distinct as the pressure is reduced. With this direction of current the striation in the small tube does not disappear, but on the contrary is quite sharp and distinct through the range from 1.5 mm. to 1 mm.

With this tube it has proved impossible to keep the current steady enough to secure trustworthy results at pressures below 0.3 mm. This seems to be due to the fact that the enlarged portion of the side tube which contains the negative electrode becomes entirely filled with the blue cathode glow, which at irregular intervals extends itself through the narrow connection into the main tube, and greatly reduces the current. This lasts for a few seconds only, when the normal conditions return.

This difficulty did not occur at all with the alternating current. Below 0.15 mm., however, the pressure decreases during the passage of the current, probably on account of the absorption of the gas by the walls, which was investigated by Willows;<sup>1</sup> and as the radiometer deflection here falls off rapidly with the pressure, this becomes a serious difficulty. The small plot in Fig. 4 gives the results of a large number of readings with the alternating current in this region, each point representing several determinations. It has little value except to show the general nature of the curve; and even this is doubtful below 0.1 mm.

A possible explanation of the lower values found with the alternating current, as shown by Fig. 3, is that the efficiency is different for the two directions of current in the tube used, being greater when it is next the anode, as used with the direct current. A series of readings with the large tube to test this point gave the following results on page 248.

Current reversed means the reverse of the direction ordinarily used. The efficiency proves to be somewhat less at the cathode end, but with the alternating current it is lower still, so this explanation is not sufficient.

Another possible reason for the difference is suggested by the fact, previously mentioned, that with the alternating current there

<sup>1</sup> Phil. Mag. (6), 1, 503, 1901.

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seems to be no current through the tube during a portion of the time. The current while flowing would thus have a larger mean value than that of the direct current which produces the same radiometer effect; and the results next presented show that the efficiency is in general smaller for larger currents, this being more noticeable in the large tube for the range of current here used.

## TABLE IV.

Current Reversed.	Current Direct.	Current Reversed.	Current Alternating
.090	.093	.090	.087
.082	.113	.100	.083
.105	.103	.094	.086
Mean .092	. 105	.095	.085

# Effect of Direction of Current.

Pressure 3.1 mm. Current 0.007 ampere.

Variation with Current.— Ångström<sup>1</sup> found that with nitrogen the efficiency was independent of the current strength through a rather wide range. Several trials through a small range seemed to show the same result for this tube. As some theoretical considerations however seemed to point to the existence of such a variation, a more careful trial was made through a wider range. This showed its existence, and also the reason why it had been overlooked before. The results for the two tubes are given in Table V., and plotted in Fig. 9.

T	37
IABLE	· •
IADLC	v

		Pressure 3.85 mm. Small Tube.		Pressure 2.6 mm. Large Tube.	
c	٤.	¢	6.	¢	<i>e</i> 1
7.0	.266	3.5	.256	7.0	.130
1.6	.290	1.6	.293	10.5	.130
10.5	.290	7.0	.264	3.5	.156
7.0	(.278)	4.5	.246		
	(.260)	7.0	.258		

c, Current in milliamperes. e, Efficiency.

The earlier trials had been made with the small tube in the neigh, borhood of 6 milliamperes where the variation happens to be small. <sup>1</sup> Wied. Ann., 48, 508, 1893.



The two bracketed values were obtained for the same current under different circumstances. For the first, e = .278, the readings were taken immediately after the tube had been used with a stronger current, which had heated it considerably. After cooling for five minutes the readings were taken which gave the smaller result. This suggests that the rise of temperature which accompanies increased current may increase the efficiency; and with the larger currents this may over-balance the decrease due to the effect of current change alone.

Variation with Temperature. - It seemed desirable to test this temperature effect by heating the tube from the outside and using a constant current. There was no obvious way to apply the heat without a radical change in the mounting of the tube; but a satisfactory result was finally obtained by using the current as a source of heat. A wooden box was fitted over the small tube, and the joints packed with wool. A current of about 12 milliamperes would heat the air in the box enough so that after stopping the current and allowing the tube to cool a few minutes to secure uniform temperature throughout, the whole would be about 20° above room temperature. The readings were then taken with the usual current of 7 milliamperes, which was sufficient to maintain the increased temperature for the necessary time. A similar determination was then made with the air in the box at room temperature, so that the conditions are the same in the two cases, except for the difference in temperature of the medium surrounding the tube. The results are:

	Table VI.	
	Pressure 2.8 mm.	
Temperature.		
40°		e = .329
21°		.323

A similar determination made several weeks later gave almost identical results. The method could not be used at lower pressures, as the heating effect of the current is not sufficient.

Total Radiation.— A special species of readings, without the water-cell, was taken to show the total radiation from the tube as a function of the pressure and of the current. The readings were taken in the order shown in Table VII. as a check against change

in sensitiveness of the radiometer or other conditions. It must be assumed that the radiometer deflection is always proportional to the total radiation per unit length of the luminous column. This is more likely to be true with the small tube than with the large, since in the latter there are more appreciable variations in the size and general appearance of the luminous column at the points of entrance and exit, as the pressure or the current is changed. The results for the large tube are less trustworthy for this reason; and in fact it was impossible to obtain any consistent readings for the variation with current.

	AB	LE	V	П.
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		1	Deflection a	and Pressur	e.		
Small Tube.				Large	Tube.		
*	d	<i>•</i>	ď	1	d	Þ	d
1.6	8.00	0.62	8.47	1.12	5.92	0.33	4.75
2.56	8.39	0.39	8.03	2.25	7.97	0.22	5.77
3.85	9.09	1.9	8.34	2.72	8.70	0.13	5.28
4.5	9.55	0.56	8.62	4.25	11.60	3.4	10.13
3.36	8.98	0.32	8.29	2.90	8.70	1.2	6.04
2.50	8.47	0.18	7.23	2.2	7.97	0.44	5.29
1.9	8.28	0.10	4.70	1.6	6.80	0.9	5.34
1.4	8.18	0.06	3.29	1.28	6.10	0.56	5.00
1.04	8.53	0.045	2.45	1.00	5.40	0.24	5.81
0.8	8.48			0.8	4.80	0.07	3.50
				0.5	4.13	0.04	2.60
		Deflect	tion and Cu	rrent. Sm	all Tube.		ni me
-	с	4	r	c		d	
1	L.6	6.	16	3	.5	10	.40
2	7.0	16.	85	1	6	5	.80
10	).5	21.	60	4	.5	12	.76
2	7.0	16.	74	7	' <b>.0</b>	16	.80

The results for change of pressure are plotted in Fig. 5.

Total Radiation -- Variation with Size of Tube. -- If it may be assumed that at a given pressure the efficiency as measured by the water-cell is the same multiple of the true luminous efficiency in the two tubes, a method suggests itself for comparing the total radiation per unit length of the two tubes. This cannot be done with the radiometer directly, for different fractions of the total radiation reach the radiometer vane in the two cases. It is only necessary to measure the ratio of luminous intensities by a photometer method, and reduce this to ratio of total intensities by using efficiency ratios.

A paraffin diffusion photometer was used for this purpose, made of two blocks of clear paraffin 2 mm. thick and 14 mm. long, separated by tin-foil. This was arranged to move in the space between the tubes so that the radiation fell upon its two faces at nearly equal angles at the final setting. The tubes were covered with black paper, leaving apertures through which one centimeter, as nearly as

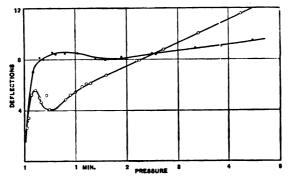


Fig. 5. Total Radiation and Pressure. Dots, Small Tube; Circles, Large Tube.

possible, of the axis of each tube was visible from a point at the center of the photometer block.

The pressures were so chosen that the luminous column in each tube was entirely continuous, and the difference in color apparently as little as possible. The alternating current from the city circuit was used. The efficiencies for the large tube, determined at the time, are somewhat higher than those shown in Fig. 4, but correspond to those of Table IV. Each result is the mean of seven settings of the photometer block, which agreed to within 0.5 mm. The distances l and s, Fig. 6, are measured from the tin-foil partition to the axes of the tubes.

The effect of the total radiation from one tube which reaches the photometer block is nearly the same as though it were all concentrated in the axis. For consider two layers at equal distances +x and -x from the axis (Fig. 6). Their distances from the photometer block are l + x and l - x; and their lengths are also propor-

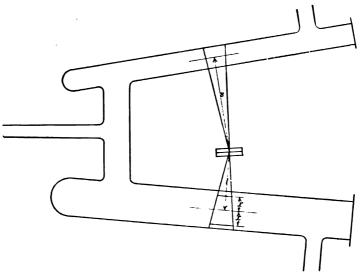


Fig. 6. Vacuum Tube and Photometer.

tional to those distances. The assumption then amounts to saying that

$$\frac{l+x}{(l+x)^2} + \frac{l-x}{(l-x)^2} = 2l/l^2$$

For the extreme case when x = r for the large tube the error is less than 5 per cent. The ratio of the total radiation per unit length for the two tubes is then computed as

$$\frac{R_i}{R_i} = \frac{l^2 e_i}{\overline{s^2 e_i}} \cdot$$

TABLE VIII.

1 L 21					
≠ (mm.)	1	5	ei	۶,	R <sub>i</sub> /R.
2.3	3.25	4.85	.135	.335	1.08
2.75	3.10	5.00	.105	.300	1.10
z	· · · · · · · · · · · · · · · · · · ·		<u> </u>		

The probable error of the results is doubtless as great as ten per cent. and to this approximation the ratio is unity.



the same dimensions. This had a fine platinum wire stretched across the middle of each branch of the tube, perpendicular to its axis, and a similar wire on each side of this, at distances of approximately 3 cm. The measurements were made by the method of condenser and ballistic galvanometer.

The condenser, a standard by Nalder Bros., has a range from 0.05 to 1.0 microfarad, which made it possible to keep the galvanometer throws within the range from 4 to 12 cm., although the differences of potential measured varied in the ratio of 1 to 16.

The D'Arsonval galvanometer used was much too sensitive, so its coil was shunted by means of a piece of German silver wire. This served the additional purpose of short-circuiting the coil and quickly damping its vibration after the condenser had been discharged through it. The complete period was five seconds, and the damping so good that three readings could easily be obtained within fortyfive seconds. The resistances of coil and shunt were afterward measured and found to be in the approximate ratio of I to 20, while the throws for equal quantities were about as I to 40. The back e.m.f. due to the beginning of the coil's motion thus greatly modifies the distribution of the current.

The galvanometer scale was calibrated directly by charging the condenser from a storage battery to a known difference of potential, measured by a voltmeter, and then discharging through the galvanometer. The data given below show that the deflection was quite accurately proportional to the potential difference for the range used, and also give an idea of the accuracy of the readings.

Calibration of	Ballistic Galvar	Condenser Charged to 76.7 Volta		
Capacity.	1.0	0.5	0.2 + 0.2 + 0.05 + 0.05	
Capacity. Throws.	9.72	4.83	4.85 .	
	9.71	4.85	4.84	
	9.69			

For capacity of 1 microfarad, 1 cm. throw = 7.9 volts.

The system of connections used, with the ordinary three-way discharge key, made it necessary to keep one galvanometer terminal continuously connected to the condenser, and so to the tube. When the cathode was at the grounded end of the line, this galvanometer terminal was raised to a potential high enough to cause a slight electrostatic action, which resulted in a slow zero drift. The uncertainty thus introduced into the readings was not often greater than one per cent. It was seldom noticed when the anode was next the grounded end of the line, as the chief drop of potential within the tube occurs at the cathode.

Connecting wires from the six platinum wires in the tube led to mercury cups in a block of paraffin made it easy to connect any desired pair of wires to the condenser terminals.

The attempt was now made to determine the potential gradient under all of the various sets of conditions for which the efficiency had previously been found. Aside from accidental variations in the composition of the air used, the only evident difference in conditions is shown by the fact that the appearance of the discharge is slightly modified by the introduction of the wires. In the unstriated discharge, each wire is accompanied by a faint stria. When the pressure is reduced until striation begins, each stria behaves as though covered by an elastic surface film, which the wires penetrate with difficulty, and hence the striæ are distorted in form, and displaced in position, where they come in contact with the wires. This was noticed by Wood.<sup>1</sup> Reducing the pressure still further until the striæ become hazy in outline, this effect disappears, and the wires have no perceptible effect upon their distribution or form. The change in potential gradient which accompanies this changed appearance is of course unknown; but the mean value for the whole tube, which is the desired result, is probably little affected.

In the tabulated summary of results, Table IX,  $V_a$  is the potential gradient calculated from the observed potential difference between wires 1 and 2,  $V_b$  between wires 2 and 3,  $V_{a+b}$  between wires 1 and 3; wire 1 being the one nearest the electrode which is next the tube used. The differences between results for the different intervals are but little greater than the probable error of observation. Such consistent results were hardly expected in the striated discharge, where the results of Graham<sup>2</sup> and H. A. Wilson<sup>3</sup> show usually a change from point to point, in passing from one stria to

> <sup>1</sup> Wied. Ann., 59, 250, 1896. <sup>2</sup> Wied. Ann., 64, 49, 1898. <sup>3</sup> Phil. Mag. (5), 49, 505, 1900.



the next, as well as a progressive increase in going along the tube from anode toward cathode. There is some evidence of the latter variation in the small tube. The mean result for each case probably corresponds nearly enough to the mean potential gradient in the discharge which affected the radiometer.

# Potential Gradients.

		Sn	nall Tube.		
Vs	Va+b	V.a.	Mean.	Þ	Vip
6.40	63.7	64.4	64.0	3.12	20.5
72.5	72.1	71.4	72.0	3.68	19.6
79.6	80.3	78.8	79.6	4.26	18.7
67.8	66.4	65.6	66.6	3.22	20.7
55.8	55.1	54.1	55.0	2.46	. 22.4
45.3	45.5	45.3	45.4	1.88	24.1
38.3	37.7	39.1	38.4	1.42	27.0
32.9	32.7	32.0	32.5	1.09	29.8
29.4	28.5	28.1	28.7	0.83	34.6
21.9	21.6	21.3	21.6	0.48	44.5
51.7	51.5	51.4	51.5	2.28	22.6
25.6	25.9	25.6	25.7	0.81	31.7
24.2	23.9	24.3	24.1	0.60	39.6
21.2	20.8	20.2	20.7	0.46	45.0
15.9	16.0	16.3	16.1	0.28	57.5
13.3	12.8	12.4	12.8	0.19	67.5
Current	t, m. a.	Mean V.	Þ		1.1
	1.6	91.5	3.68		24.7
	3.5	80.6			21.8
	4.5	76.5			20.7
	7.0	71.0			19.3
	10.5	68.0			18.4
	(11.	38.3	1.54		
Striated	5.5	41.0	. "	)	
Discharge	111.	24.3	0.71		
	5.5	26.3	**		
Te	mperature.		V		¢
	20°		58.0		2.74
	41		57.5		
	20	1	59.0		
	40		57.6		

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Large Tube.							
Vo	Va+b	Va	Mean.	*	VIP		
55.3	55.8	55.5	55.5	3.12	17.8		
63.0	63.5	62.3	62.9	3.68	17.1		
68.6	68.1	68.3	68.3	4.26	16.0		
56.0	56.7	57.7	56.8	3.22	17.6		
47.6	48.3	48.2	• 48.0	2.46	19.5		
39.3	39.8	39.9	39.7	1.88	21.1		
32.7	32.1	32.4	32.4	1.42	22.8		
27.6	27.6	27.6	27.6	1.09	25.4		
23.4	22.9	22.4	22.9	0.83	27.6		
15.8	15.8	15.5	15.7	0.48	32.2		
39.5	39.2	39.8	39.5	1.79	22.0		
27.3	26.9	27.9	27.1	1.06	25.5		
19.3	18.7	19.0	19.0	0.61	31.1		
14.4	13.8	13.7	14.0	0.38	36.4		
11.1	11.1	11.2	11.1	0.23	47.3		
8.5	8.4	8,4	8.4	0.16	53.0		
Current, m. a.		V	V Þ		VIÞ		
3.8 ·		58.2	2.64		22.1		
4.5		56.0			21.2		
7.0		52.4		1	19.3		
10.5		47.7		i i	18.1		

TABLE IX.—Continued.

These results are in general agreement with similar ones obtained by Herz<sup>1</sup> and Schmidt<sup>2</sup> for nitrogen, with the single exception that the latter finds, in the case of the striated discharge, an increased potential gradient with increasing current, while the opposite is true in the present case.

#### DISTRIBUTION OF ENERGY IN THE SPECTRUM.

Through the kindness of Mr. W. W. Coblentz I was enabled to use his spectrometer, with rock-salt prism and radiometer,<sup>3</sup> in the attempt to learn something about the distribution in the spectrum of the energy which affects the radiometer. The energy is so small that it was necessary to use wide slits in front of the tube makes it impossible to do more than find the approximate location of the principal maxima, and get a general idea of the distribution. The small tube was used, and the pressure kept at approximately 0.9 mm. The heating effect is small at this pressure, so that a stronger current could be safely used, and a small pressure change causes little change in the amount of the total radiation. The alternating city circuit was used for convenience, so its strength could not be readily measured. It was probably as much as 15 milliamperes. As the collimator was moved to throw different regions of the spectrum on the radiometer slit, the vacuum tube had to be adjusted by hand, which may have caused some uncertainty in the readings; and the current was by no means constant.

The curve, Fig. 7, shows the observed deflections in millimeters on a scale at 150 cm., wave-lengths being obtained from the cali-

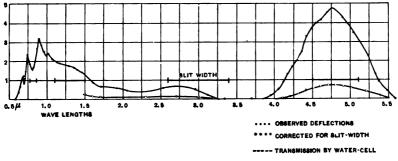


Fig. 7. Spectrum Distribution of Energy.

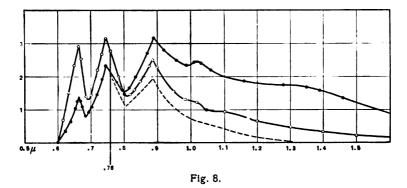
bration curve prepared by Mr. Coblentz. Fig. 8 shows the region out to  $1.5 \mu$ , plotted on a larger scale of dispersion. The zero was nearly always unsteady, which made the smaller readings uncertain. Each point represents the mean of three or more readings, taken at favorable times when the conditions seemed best. The whole region as far as  $7.5 \mu$  was covered consecutively in one day; and some days later the region from  $0.6 \mu$  to  $1.5 \mu$  was explored again, with results almost identical as regards the location and relative magnitude of the maxima.

The curve shows well-defined maxima at wave-lengths 0.66, 0.74, 0.89 and 4.75; while less prominent ones are indicated at 1.02, 1.40, 2.75 and 4.4.

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Each of the slits was 1 mm. wide; and this width, expressed in wave-lengths, is shown by a horizontal line, for various regions of the spectrum. The observed curve is corrected for slit-width by means of the formula given by Paschen,<sup>1</sup> using the first two terms of the series. The ordinates to this corrected curve are chosen merely to give a convenient scale.

If it be assumed that this corrected curve properly represents the distribution of energy, it is of course possible to compute the true luminous efficiency, as the ratio of that portion of the area to the left of the ordinate  $0.76 \mu$  to the whole area. The reliability of this



result may be roughly checked by computing in a similar way the water-cell efficiency, and comparing this result with that obtained by the direct method. For this purpose Prof. E. L. Nichols has kindly allowed me to use some unpublished data on the transmission of the water cell, which show that it is approximately 0.85 through the visible spectrum, and then falls to nearly 0 at 1.5  $\mu$ . The dotted curve is obtained by applying these transmission ratios to the ordinates of the corrected energy curve from 0.76  $\mu$  on. Then the area included under this curve, plus eighty-five per cent. of the visible energy previously obtained, is taken as the energy which would get through the water cell.

The results are 0.18 for the luminous and 0.42 for the watercell efficiency. These are too low, however, because the losses due

shorter wave-lengths. The only available data for determining the rock-salt loss are some observations by Mr. Coblentz on a thin plate, with surfaces in about the same condition as those of the prism, as regards lack of polish. These show a diminished transmission of about twelve per cent. from  $4.5 \mu$  to  $1 \mu$  and of nearly twenty per cent. to  $0.7 \mu$ . A detailed correction of the curves on this basis is hardly warranted. A reasonable estimate, including the effect of the silvered mirrors, is that the water-cell efficiency as given above should be increased about ten per cent., and the luminous efficiency about fifteen per cent., which would make the numbers forty-six and twenty-one respectively.

This result for the water cell is apparently too large, when compared with the value 0.41 given by the curve in Fig. 4; but on account of the stronger current here used the efficiency would be increased to a value perhaps even higher than this, according to the lower curve of Fig. 10. The two results are thus in agreement as nearly as can be determined. It then follows that 0.20 is a good approximate value for the luminous efficiency under the working conditions, which is at least not too large.

It is to be noted that in the curve of observations, Fig. 7, the maximum at  $4.75 \mu$  has very nearly the form which would be given by a single line in the spectrum at that wave-length. It is approximately a triangle, whose base is twice the slit-width. Nearly the whole energy in this portion of the spectrum thus seems to be concentrated in a single line, or at least a narrow band or group of lines.

In testing the practicability of a suggestion that a carbon bisulphide prism might be used to advantage with this radiation, it had been found that a layer of carbon bisulphide not more than 3 mm. thick, between quartz plates, produced an absorption comparable with that of the water cell. This is now explained by the fact that carbon bisulphide has a strong absorption band at about  $4.7 \mu$ , as was found by Mr. Coblentz in the course of an investigation soon to be published.

This radiation comes from air, which contains traces of mercury, from the pressure gauge, and of hydrocarbons, from the oil in the pump and the grease in the joints.

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## THEORETICAL.

According to the electron theory in its present form, the ordinary gas molecule is thought of as an aggregate of particles carrying electric charges, which must be positive and negative in equal amount, since the molecule as a whole is electrically neutral. It is possible to separate from the molecule a minute particle which carries a negative charge, and thus leave with the remainder of the molecule an equal positive charge. This negatively charged particle, or electron, carries a charge equal to that of the hydrogen ion in electrolysis, as was shown by Townsend.<sup>1</sup> From the measured value of the ratio of charge to mass, and the magnitude of the charge, which has recently been determined by J. J. Thomson<sup>2</sup> and H. A. Wilson,<sup>3</sup> the computed mass of the particle is about 1/700 as great as that of the hydrogen atom. And this is independent of the kind of matter from which it comes.

Whether the remainder of the molecule is an aggregate of similar small particles is still an open question, so far as the writer is aware; and it is perhaps immaterial for our present purpose.

We are then to think of the positive column of our vacuum tube, when the current has been established through it, as occupied by gas molecules, a certain small number of which have been dissociated in this way. These dissociated particles will have, beside their ordinary gas motion, a component motion along the length of the tube, produced by the electric forces. The positive and negative charges being equal, the forces will be the same; but the negative will acquire much greater speed in the same distance, on account of the smaller mass with which they are associated. Each will, however, acquire the same energy in moving through the same difference of potential.

This motion will be frequently interrupted by collisions with neutral molecules which are moving at random. The mean free

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somewhat toward the condition of particles moving through a field of similar particles at rest. The negative electrons will have a longer free path, because of their smaller size; but it probably cannot be computed directly, since the size here means the diameter of the sphere of action, and this differs from that considered in the kinetic theory, in that it depends upon the electric forces chiefly.

The mean energy at collision, in any case, will be that acquired by the charged particle in moving through its path under the action of the electric forces. When such a collision occurs, a part of this energy will be transferred to the molecule struck, where it will in general produce two effects. The first is an increase in the kinetic energy of the molecule as a whole, which, considering all such effects, means a rise in the temperature of the gas. The second is an effect within the molecule itself, producing relative motion among its parts. As these parts carry positive and negative charges, and are probably held together in a coherent system by the electric forces acting between them, such relative motion will be vibratory in character, and hence a probable source of electromagnetic radiation. The intensity of such radiation would vary with the energy of collision, which is greater for the negatively than for the positively charged particles. J. Stark<sup>1</sup> has suggested that the negative electrons, on account of their smaller size, are able to act selectively on the component parts of the molecule, and so cause much greater vibratory motion compared to the motion of the whole molecule, than the positive particles; so that the latter may be left out of account in considering intensity of radiation. Whether this is true or not will make little difference in our application of the theory.

It is of course possible that a collision may occur with sufficient energy to cause dissociation of the molecule struck, thus producing a new pair of charged particles. Townsend has succeeded in measuring the number of such dissociations produced by a negative electron in passing through one centimeter of gas, with various pressures and potential gradients. The results applied to the conditions which obtain in the positive column of a vacuum tube<sup>2</sup> show that the proportion of collisions which produce dissociation is exceedingly small, so that this feature of the case need not be considered.

> <sup>1</sup> Die Electrizität in Gasen, Stark, p. 444. <sup>2</sup> Phil. Mag. (6), 1, 226, 1901.

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According to this view, radiation from a gas due to an electric current through it, differs from that due to high temperature chiefly in the fact that the source of the radiation, namely the vibratory motion within the molecule, is caused in the latter case entirely by collisions between the molecules, while in the former case it is caused by collisions between molecules and charged particles, which are for the most part much smaller than molecules, and are moving at relatively high speeds. In the first case the energy increases with the temperature, in the second with the potential gradient; the density of the gas being supposed constant.

Since with high temperature radiation the efficiency, or proportion of high-frequency radiation, increases with the temperature, or with the energy of the collisions, it seems likely that the efficiency of the electrical radiation should also increase with the energy of collision, which is measured by the product of potential gradient and mean free path. J. Stark<sup>1</sup> has proposed this view, and applied it to Ångström's results. It will now be applied to the results previously described.

Variation with Pressure. — The energy of collision will vary with Va, where V is potential gradient and a is mean free path. If the temperature of the gas be assumed to remain constant and the pressure to vary, Va will vary with V/p.

In Fig. 9 the values of V, and also of V/p, are plotted for the two tubes. Comparison of the latter with the efficiency curves of Fig. 4 shows that the variation is in the right general direction for each tube separately. If, however, the efficiency is a function of Vaonly, a given change in the value of Va, no matter how produced, should cause the same change in the corresponding efficiency ratio. Starting with Va or V/p, in the large tube at 3 mm. pressure, its value may be increased by going to the small tube at the same pressure, or by reducing the pressure in the large tube; and equal changes produced in this way are not accompanied by equal changes in the efficiency ratio. This point will be referred to again, after

mains nearly constant when the temperature rises. The mean free path will then be determined by the density, and its change may be calculated from the temperatures. These are unfortunately not known under the conditions of the experiment; if Wood's results<sup>1</sup>

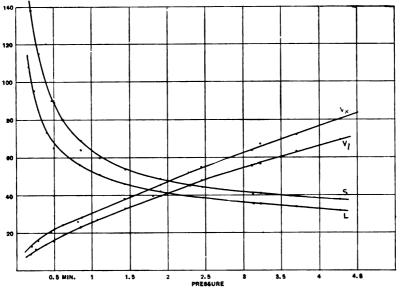


Fig. 9. V, V<sub>2</sub> Potential Gradients. Ordinates = volts per cm. S, L, potential gradients  $\div$ - pressure. Ordinates = V / p  $\times$  2.

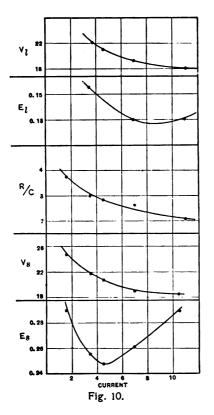
for nitrogen may be assumed to hold to the same order of magnitude, the temperature corresponding to the data of Tables VI. and IX. may be as high as  $450^{\circ}$  absolute. The ratio of the values of Vawould then be 470/450 575/583 = 1.03; and the ratio of efficiencies is .339/.323 = 1.05. The same change of 3 per cent. in the value of V/p at this pressure, 2.75 mm. (Fig. 9), corresponds to a pressure difference which would change the efficiency (Fig. 4) in the ratio 1.0375. The variation is thus in the right direction, and as nearly the right amount as could be reasonably expected under the experimental conditions.

Variation with Current.—In Fig. 10 are plotted the results obtained when the current is varied at constant pressure (Tables V. and IX.). The potential gradient curves show the variation in V

<sup>1</sup>Wied. Ann., 59, 244, 1896.

simply, since p is constant. *a* varies with the temperature, as in the case considered above, but in a less known way; so that calculations similar to the one given there are of little value. Using the slopes of the curves at the smallest current, where the temperature variation is small, results are obtained of about the same order of accuracy as those for the variation with temperature.

Total Radiation. — It was mentioned above that the energy transferred to the molecules during collisions is manifested partly by rise



of temperature of the gas, and partly as radiation energy. When constant current is used. the potential gradient measures the supply of energy; and comparison of Figs. 5 and 9 readily shows that the radiation represents different fractions of the total energy at different pressures. Ångström<sup>1</sup> obtained an absolute measure of the radiation energy, and so found the values of these fractions. For nitrogen, they vary from 0.025 at 1.6 mm. to 0.075 at 0.12 This variation doubtless mm. has some effect on the efficiency ratio.

If however the pressure be kept constant and the current varied, this variation will not enter, and the total radiation should be proportional to the

product of potential gradient and current strength; or potential gradient should vary with radiation divided by current strength. This latter quantity, R/C, is plotted in Fig. 10 for the results of Table V. and bears out this relation approximately, on comparing with the potential gradient curve just below. Temperature does not enter here, and so its variation causes no trouble.

<sup>1</sup> Wied. Ann., 48, 524, 1893.

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This consideration, when applied to the total radiation per unit length of the two tubes, at the same pressure and current, shows that it should be in the same ratio as the potential gradients, and hence slightly less for the large tube. The results obtained by the photometer method, Table VIII. make it a little greater; but the difference is probably not greater than the experimental error.

Returning now to the consideration of the results shown by Figs. 4 and 9, it is evident that a comparison on the assumption of constant temperature is not legitimate. Heat is developed at nearly the same rate in the two tubes, and so the temperature must be much higher in the smaller one. If this be assigned a temperature  $200^{\circ}$  above the normal, the temperature in the large tube would be about  $50^{\circ}$  above. And this temperature difference would reduce the difference in efficiencies by perhaps forty per cent. of the larger. No conclusions can therefore be drawn as to the application of the theory to these results unless the temperatures of the gas within the tubes be measured. This the writer hopes to be able to do in the near future.

## SUMMARY.

The chief results of the investigation may be briefly summarized as follows :

I. The theory that the radiation from a vacuum tube is due to collisions between charged particles and neutral gas molecules, and that the proportion of high-frequency radiation increases with the energy of these collisions, is sufficient to account for the observed facts in all cases where the conditions are well enough known to warrant its application.

2. The luminous efficiency of vacuum-tube radiation by air at a pressure of 1 mm., under the conditions described, is approximately 0.20.

3. A considerable portion of this radiation is due to a single line, or narrow group of lines, at wave-length  $4.75 \,\mu$ .

It gives me pleasure, in concluding, to express my thanks to Professor Nichols, who suggested the investigation, and to Professor Merritt and Dr. Shearer, for their helpful suggestions as well as for the material facilities which they have placed at my disposal.

I am also greatly indebted to Mr. W. W. Coblentz for the privilege of using his apparatus, and also various results which he has obtained with it.

PHYSICAL LABORATORY OF CORNELL UNIVERSITY, May, 1903.



## ON ELECTRIFICATIONS PRODUCED BY GASES THAT HAVE BEEN EXPOSED TO ROENTGEN RAYS.

### BY JOHN ZELENY.

1. Some years ago 1 I showed that when a piece of metal is surrounded by air which is partially ionized from exposure to Roentgen rays it acquires a negative charge, while the air itself becomes positively electrified. I showed how these charges could be augmented by increasing the surface of the metal that is exposed to the air and blowing the charged gas away from it. The explanation offered for the formation of the charges was based on the following considerations : It was found<sup>2</sup> that the oppositely charged ions formed in air by Roentgen rays have different migration velocities when in an electric field, and as the negative ions move the faster it was concluded that these ions are smaller in size than the positive ones. When the ions from a gas impinge on a bounding wall they give their charges to it, and so the concentration of the ions near the wall becomes less than it is in the body of the gas. On account of this difference of concentration the ions diffuse from the body of the gas to the wall, and as the negative ions diffuse the faster the bounding wall becomes charged negatively, while the excess of positive ions remaining temporarily in the gas gives it its positive charge.

More recently Villari<sup>3</sup> has carried on a large number of experiments with Roentgenized air blown through straight and coiled tubes, and through bundles of wires, gauzes and metal foil. Depending upon the conditions, the charges given to the metal in these cases were sometimes positive and sometimes negative. To explain his results, Villari has offered the hypotheses that when Roentgenized air passes by a metal surface the friction produces

<sup>1</sup> Philosophical Magazine, XLVI., 1898, p. 134:

a separation of the two electricities, that the positive electricity appears on the metal surface when the friction is above a certain amount while with less friction the metal becomes negative, and that the electricity of the opposite sign does not remain in the air but is used up in changing the Roentgenized air into ordinary air.

In the present paper, Villari's results and hypotheses will be considered in conjunction with some new experiments which have been performed, and it will be shown that all of the results find a general and simple explanation in ascribing their cause to the unequal size of the ions of opposite sign which are present in the gas.

2. For a clearer presentation of the subject, the experimental results will be deferred and a purely theoretical case will be considered first.

Suppose that AE (Fig. 1) represents a long, metal tube, through

Α	В	с	D	E
		Fig. 1	Ι.	

which a gas is made to flow in the direction from A to E. Suppose further that the gas entering at A contains an equal number of oppositely charged and uniformly distributed ions, of which the negative are the smaller and consequently the more mobile. As the gas passes along the tube, the ions gradually disappear from it because of the recombination of those of the opposite kind and because they discharge themselves when they come into contact with the walls of the tube. In the first part of the tube the negative ions, being the more mobile, diffuse the more rapidly to the walls of the tube, giving it a negative charge and leaving the gas itself charged positively. But as the gas passes along the tube the preponderance of the negative ions reaching the walls gradually gets smaller both on account of the relatively greater number of the positive ions remaining in the gas and because this excess of the positive gives rise to electrical forces that tend to drive them to the

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for this depends upon its cross-section and upon the velocity of the stream of air, increasing with both of these quantities. The gas issuing from the tube has lost its conductivity and is electrically neutral. The tube as a whole does not become charged, as the amount of positive electricity received must equal the amount of the negative, since the gas entering and leaving the tube is assumed to be without a charge.

3. The result of a number of modifications of the conditions can now be stated.

(a) If the tube is made shorter than AE and the velocity of the gas stream is maintained as before, the gas issuing from the tube will be charged positively while the tube itself will get a negative charge.

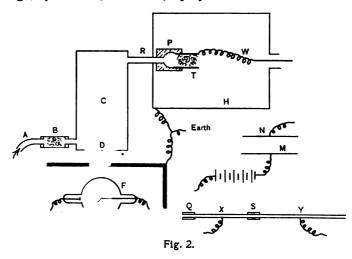
(b) If the tube is divided at B and the two parts insulated from each other the gas issuing from E will be neutral, the part BE will get a positive charge, and the part AB a negative charge.

(c) In the preceding case a piece DE of the tube may be removed such that the negative charge received by the part BC is just equal to the positive received by the part CD, so that the part BD as a whole will not become charged. The gas issuing from D will have a positive charge.

(d) If in the preceding case a piece of tube longer than DE is removed, the negative charge reaching the remainder will be greater than the positive and the tube will now become negatively charged while the gas issuing from it will be positive as before.

4. In any actual experiment where the air is exposed to the Roentgen rays in one vessel and from there blown into any tube under consideration, it is evident from the above that when it enters such a tube it will have a positive charge because the diffusion process has been going on before the air reaches the tube. This charge carried by the air into the tubes employed by Villari was left out of account by him although it seems that it played an important part in some of his experiments.

To make the matter more conclusive an experiment will be described which shows that such a positive charge does actually exist in the air as it enters the tube in an apparatus similar to that used by Villari. The main parts of the apparatus used for the experiment are shown in Fig. 2. The air was sent from a large gasbag through the tube A and through the plug of glass wool B into the large, cylindrical, tin can C, 15 by 28 cms. in size.



From C the air passed through the short brass tube R and out through a plug of glass wool contained in the short brass tube T, zcms. in diameter. The tube T was held and insulated by the paraffin tube P and was connected to one pair of the quadrants of an electrometer by the wire W. While in the can C the air was exposed to Roentgen rays which came from the bulb F and entered at the paper or aluminum window D. The rest of the apparatus was shielded from the rays and electrically protected by earthed metal screens.

It is well known<sup>1</sup> that the ions produced in gases by Roentgen rays are all removed by passing the gas through a plug of glass wool such as that contained in the tube T. So, by passing the gas through the above apparatus the electrometer indicates whether the gas coming out of the tube R is electrically neutral or whether it is charged with electricity of either sign.

On performing the experiment it was found that when air was used it always came out charged positively. The maximum

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velocity of the gas stream, and upon the length of the insulation at P. Since the charge on the tube T is gradually dissipated by conduction through the ionized gas that approaches it through P, the charge reaches a fixed value when the rate of its acquisition is equal to the loss by conduction. For a given charge on T the leakage through the gas increases with the strength of the electric field between T and R and so is the smaller the greater their distance apart. It is on this account that the maximum charge retained by T increases with the length of the insulation at P.

In Villari's experiments an arrangement similar to that above was used, the point to which his experimental tubes were attached corresponding to that occupied by T, and hence it is concluded that the gas entering the tubes in his experiments was always charged positively. In any of his experiments, therefore, where the larger part of the ions diffused from the gas to the walls of the tubes, a resultant positive charge was necessarily obtained.

5. In one series of his experiments Villari found<sup>1</sup> that when he passed the Roentgenized air, coming from a can similar to C above, through a short tube this received a negative charge but when the air was passed through a long tube the charge acquired was positive. An explanation for this is readily seen from the considerations given in §§ 2 and 3, where it was shown (case d) why a short tube should acquire a negative charge, and (case b) why a long tube should become positively charged.

6. Villari found that air blown through a tube wound in a number of turns loses its conductivity more rapidly than if it goes through the same tube when straight. I performed some experiments with various lengths of rubber tubing interposed at the point R in the apparatus shown in Fig. 2. On blowing the Roentgenized air through these tubes both when straight and when coiled the charge received by T was positive in all cases.

P and T were then replaced by the two parallel plates M and N shown in the figure. M was kept at a potential of ten volts by a battery and N was connected to the electrometer. The conductivity of the gas issuing from R was measured by means of these plates.

In one case when the rubber tube placed at R was 90 cms. long and 6 mm. internal diameter, the charges received in one minute by

<sup>1</sup> Rend. Lincei, 1900, p. 13.

the plate N when the tube was arranged in one large loop were + 65 electrometer divisions with M positive and - 45 electrometer divisions with M negative. When the same tube was wound in eight small loops the deflections obtained were + 13 divisions with M positive and - 4 divisions with M negative.

With a straight tube 19 cms. long the deflections averaged 166 divisions for the same time, while when the tube was made 230 cms. long the deflections were just barely appreciable. It is noticed from the numbers first given that there was an excess of positive ions coming from the tubes.

The greater loss of conductivity in passing through a tube wound in several loops is to be explained in the following way. When a tube is nearly straight the motion of the gas through it is steady, with the various portions of the gas moving in lines parallel to the axis of the tube. If, however, a tube is much curved, the conditions for steady motion no longer obtain and the motion is turbulent. With steady motion the ions from the center of the tube can get to the walls but slowly by diffusion. With turbulent motion, however, the ions are carried by the eddies from the center to the walls and so are discharged more rapidly.

Dorn<sup>1</sup> has offered an ingenious explanation for the positive charge that a tube takes on when it is wound in a coil and Roentgenized air is passed through it. He suggests that the ions maintain their direction in turning a corner on account of their relatively large mass, and as the mass of the positive ions is the larger, that more of these strike against and are discharged to the walls. But a straight tube if long enough also receives a positive charge under the same conditions and Dorn's explanation does not hold for such a case.

It seems rather that the charge observed in all such cases is that which enters the tube with the gas, as explained in § 4. This charge accumulates on the tube, if this is long enough for the ions to discharge to its walls while the gas is passing through. A shorter tube suffices if it is coiled since the ions discharge more rapidly in it, owing to the turbulent motion.

7. Villari found that the conductivity of the Roentgenized air is

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air stream into small channels, thereby increasing the discharging surface and diminishing the distance that the ions have to go to diffuse to the walls, and this aided in some cases by the turbulent motion produced, at once accounts for the diminished number of ions that gets through any such an arrangement.

He also finds that the rolls of gauzes become charged positively if they are long and closely pressed, and that they acquire a negative charge if they are short and loose.

Likewise, coarse copper turnings become positive when they are pressed compactly in a tube and become negative if they are put in loosely.

In all cases where the air, when it leaves the apparatus, has passed through only the first stages of the diffusion process explained in § 2, the metal parts receive a negative charge, while if the diffusion of the ions has already approached the last stages then these metal parts get the positive charge which enters the tube from the ionizing can (see § 4).

8. Villari sums up his results with the statement that all metals become charged positively when the air rubs over them with a certain amount of energy, and that they become charged negatively when the air rubs with less energy.

This statement fits all of his experiments but it will not apply to all cases. For instance, in one of my experiments the glass wool in the tube T of Fig. 2 was replaced by a roll of brass foil. On blowing very gently through this it acquired a positive charge, while for a more rapid stream it became charged negatively. Here with more energetic friction the charge was negative which is the opposite of what Villari's statement requires. The result is explained by considering that with the very slow motion the ions have so nearly all diffused out of the gas for the case to come under d, § 3, while for a faster stream case b applies.

In agreement with the ideas presented in § 2 and § 3, it was found that the gas coming out of such rolls of foil is invariably charged positively, no matter whether the foil itself is getting a positive or a negative charge.

9. Another experiment will be cited as evidence against the idea that the sign of the charge received by a tube depends upon the amount of friction of the air passing through it. The parts P and T of the apparatus shown in Fig. 2 were replaced by the arrangement QXSY shown at the side of the figure.

Here X and Y are pieces of brass tubing 2.5 mm. in diameter and 14 and 42 cms. long, respectively. The ebonite piece S insulates X from Y and the whole is attached to and insulated from R by the ebonite piece Q. One of the tubes was always connected to the electrometer and the other to earth. When the Roentgenized air was sent through these tubes with a velocity within a certain range, X received a negative charge and Y received a positive one. As the velocity of the gas was the same through both tubes and these were of the same diameter the air friction must have been the same in both; and yet the charges received by them were of opposite sign.

An explanation is at hand if we consider that in the tube X the negative ions are still diffusing to the walls in excess while in Y the positive ones predominate, the two tubes corresponding to the parts *BC* and *CD*, respectively, of the tube shown in Fig. 1.

10. One of the strongest confirmations of the explanation given for the various results that have been considered, *i. e.*, that the observed effects are due to the unequal size of the ions of the two kinds, is found in the experiments performed with carbonic acid saturated with water vapor. When I determined the ratio of the velocities of the two ions produced in gases by Roentgen rays,<sup>1</sup> the effect of the presence of water vapor in the gas upon the ionic velocities was not known. The results obtained showed that in air the negative ions move the faster while in the undried carbonic acid that was used the velocities of the two ions were practically equal. So at that time,<sup>2</sup> in connection with the experiments already referred to in § I where the charge carried by air after coming through a roll of metal foil was found to be quite strongly positive, the same experiment was performed with the carbonic acid. With this gas No. 5.]

More recently <sup>1</sup> I have determined the absolute velocities of the two ions separately in a number of gases both when dry and when saturated with water vapor. It was found that the velocity of the positive ions in carbonic acid that is saturated with water vapor is greater than that of the negative, while in dry and moist air and in dry carbonic acid the negative ions have the greater velocity. If the inequality in the size of the two ions is the cause of the electrical charges under consideration then the charge to be obtained in any case with carbonic acid that is saturated with water vapor should be opposite in sign to that obtained with air or dry carbonic acid.

For this reason Dorn suggested to Villari<sup>2</sup> that he repeat some of his experiments using moist carbonic acid instead of air. In doing so Villari obtained in two cases a charge of the same sign as with air, although it was much smaller. In a third case the carbonic acid gave a slight and uncertain charge where air gave a strong positive charge.

The results of the experiments that I performed, which will now be considered, are not in agreement with those of Villari.

The carbonic acid used was taken from a cylinder of commercial, liquid carbonic acid. For saturating the gas with water vapor it was first bubbled through the water in a large bottle containing a large number of glass rods, and then passed through a long horizontal tube half filled with water. To dry the gas it was passed through a tube of calcium chloride.

An apparatus equivalent to that shown in Fig. 2 was used. The brass tube T was somewhat longer, contained glass wool as before, and was connected to the electrometer. It was joined to and insulated from R by a piece of ebonite tubing. At its other end it carried a second piece of ebonite tubing from which a rubber tube led to a second large gas-bag. The gas could thus be made to pass from the first gas-bag through the drying or moistening apparatus,

by a second passage through the proper substance. It will be noticed that in this experiment, as explained in §4, the charge gathered by the glass wool is that left in the gas because of the faster diffusion of the ions of the opposite sign to the walls of the vessel C and the connecting tube R.

The following results are given as typical of a number of experiments performed on different days. The readings are given with their proper signs in terms of divisions of the electrometer scale, the time that the action had gone on being indicated in each case.

Time.	Dry Air.	Moist Air.	Dry Carbonic Acid.	Moist Carbonic Acid.		
30 seconds.	+ 59	+ 12	+ 29	- 19		
60 ''	+130	+ 25	+ 62	- 39		
90 ''	+196	+ 36	+ <b>93</b>	- 57		
120 ''	+256	+ 46	+126	- 73		
-						

It is seen that the charge received by the glass wool was positive in all cases except when moist carbonic acid was used, in which case the charge was negative. As stated, in this last gas the positive ions are the smaller while in all of the other cases they are the larger.

Although the same weights of 100 lbs. were placed on the gas-bag in each case, the two results for either gas are not numerically comparable as the velocity of the gas stream was not the same in the two cases, more resistance being offered to the gas in bubbling through the water than in passing through the drying tube.

The above experiments were varied by replacing the glass wool with a loose roll of brass foil and dispensing with the second gas bag, so that the gas issued directly into the open air. The brass roll was connected to the electrometer and when dry or moist air or dry carbonic acid was passed through it from the ionizing can the charge received by the roll was negative, but when moist carbonic acid was used the charge received was positive. These results are likewise explained by the faster diffusion of the smaller ions in each case to the walls of the roll of brass foil. It should be remarked that when dry carbonic acid was used after the moist had been employed a considerable quantity of the gas had to be passed

through the apparatus before the moisture was all taken up from its walls, and likewise in using the moist gas after the dry it seemed at first to lose some of its moisture to the tubes and apparatus, so that the reversal of the charge obtained did not begin until the gas had been flowing for some time. This last would indicate that the gas has to be quite near to the saturation point before the negative ions become larger than the positive. I cannot account for Villari's failure to get the reversal of effects with the moist carbonic acid otherwise than by supposing that his gas did not contain enough water vapor to produce the reversal in the relative dimensions of the two ions.

II. The unequal diffusion of the two kinds of ions has been given as the general cause of the electrifications that have been considered. There are doubtless other causes which under special conditions produce or modify to a greater or less extent the charges that are obtained. It has been known for some time that when two different metals are used, an ionized gas will produce charges upon them by the reduction of the contact difference of potential.

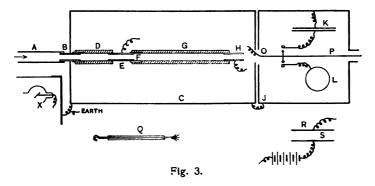
It is thought possible that the amount of the surface layer of gas on a metal may influence the charge that is received by ionic diffusion, and that this charge may on this account differ in amount for different metals.

In a recent paper<sup>1</sup> J. C. McLennan and E. F. Burton consider radioactivity as a cause for the charging of metals.

12. One of the hypotheses, already mentioned in \$1, which Villari offers to explain some of his experiments,<sup>2</sup> is that when Roentgenized air is changed into ordinary air this is done at the expense of an electric charge which vanishes. The generally accepted view of the process whereby a gas loses its conductivity is that the ions which give the gas this conductivity disappear from it either because of the recombination of those carrying opposite charges or because of their discharging themselves against some surface whither they have been carried either by electrical or mechanical forces. does not require any such a strange assumption as the destruction of an electric charge.

One of the experiments upon which Villari bases his hypothesis will now be considered. In this he took a tube of paraffin and gave its inner surface a static charge of either sign. On blowing Roentgenized air through the tube he found that the air lost its conductivity and the paraffin tube its charge. If I understand him rightly, he reasons that since the charge lost by the paraffin was not blown out of the tube with the air and since the air lost its conductivity in passing through the tube that therefore the charge had been used up in transforming the Roentgenized air into ordinary air.

But if the charge is not carried out of the tube in the direction in which the air is moving, there is still the possibility that the ions in the gas may carry it out backwards against the air stream. That this is what actually takes place in such a case was proven by means



of the apparatus shown in Fig. 3. Here G is an ebonite tube 17.5 cms. long, having an internal diameter of 1.6 cms. It carries at one end the short brass tube H and at the other end the brass collar F, by means of which it can be readily attached to the brass tube E without the development of any static charges. E is carried and insulated by the ebonite tube D. Air, blown from a gas-bag or bellows into the cardboard tube A is there exposed to the Roent-

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G is the non-conducting tube from the inner surface of which a static charge is made to disappear by blowing Roentgenized air through the tube, and it is the object of the experiment to find out what becomes of this charge.

The metal rod Q, covered with an ebonite tube and carrying a metal brush at one end, was used for charging G. The rod was connected to one pole of a small static machine and the tube G was slid over it so as to receive the discharge from the points of the metal brush on its inner surface.

The conductivity of the gas issuing from the tube H could be tested by placing at O the two plates R and S, one of which was connected to a battery of cells and the other to the electrometer. When the inner surface of G was given a charge of either sign, the Roentgenized air that entered the tube was found to lose its conductivity by passing through it and did not recover it completely until G had lost all of its charge. In the meantime E was found to receive a charge of the same sign as that given to G while Hreceived a charge of the opposite sign. Both of these charges at first sent the electrometer deflection off the scale rapidly, but the charge going to E was much the larger of the two. It will be shown that the charge received by E was equal in amount to the charge originally given to the tube G and, as has been said, it was of the same sign. The charge received by H results from the change in potential of H owing to the removal of the charge from This last fact was proved in the following manner: In order *G*. that the total charge received by H might not deflect the electrometer off the scale, the sensibility of the instrument was diminished by joining the wire leading to it to an induction plate situated above one of the quadrants, instead of connecting it directly to the quadrants as was done before. If during the charging of G the tube Hwas kept insulated and when G was introduced into the apparatus H was connected to the insulated induction plate, the electrometer showed a deflection of the same sign as that of the charge on Gowing to the charge induced on H by that on G. That is, H had a bound charge of the opposite sign to that on G and the equal free charge of the same sign as G produced the deflection on the electrometer.

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When the Roentgenized air was now blown through the tubes of the apparatus, the electrometer deflection gradually diminished and the reading on the scale finally became stationary at practically the zero position. Hence during the experiment H actually received no appreciable charge, but the removal of the charge from G simply allowed the two induced charges to reunite. This shows that in the former experiments, where H had been brought to zero potential before the Roentgenized air was sent through the apparatus, the charge of the opposite sign to that of G that was indicated by the electrometer was due to nothing more than the liberation, by the discharge of G, of the induced charge that H possessed.

The following procedure was pursued to show that the charge received by E was equal to the charge first given to G. A capacity K of .02 microfarad and a hollow cylinder L were connected by the keys indicated in the figure to the wire OP leading to the electrom-The large capacity was necessary to keep the deflections eter. on the scale. The cylinder was used to measure the charge initially given to G by the static machine. An opening in the box J above the axis of L was uncovered and the charged tube G was carefully lowered into the cylinder. The deflection of the electrometer indicated the total charge on the tube. G was then placed into its position in the apparatus, and E was connected to the electrometer and Hto earth. The Roentgenized air was next passed through the apparatus and the electrometer deflection noted from time to time. As an example of the results obtained the following readings, among the best obtained, are given.

When the tube G was lowered into the cylinder L the deflection obtained for its charge was + 132 divisions. With G in the apparatus and E connected to the electrometer the readings obtained, after the gas had been passing for the times indicated, were :

+ 2	20 d	livisions	s in	1	minute.
+ 5	66	**	" "	3	minutes.
+ 9	2	" "	**	5	**
+12	23	**	"	7	* *
+ 12	29	**	"	8	**
$\pm 12$	29	" "	**	9	**

### No. 5.] ELECTRIFICATION BY GASES.

It is seen that the charge received by E was practically equal to the charge lost by G. These is therefore no annihilation of electricity here. The charge is, as it were, simply transferred by the conducting gas from G, against the gas stream, to E. The gas loses its conductivity in the same way as in all cases where it passes through an electric field. As the ionized gas comes out of E it enters the electric field existing between the charges on G and E. The ions with charges opposite to that of G travel to G and gradually neutralize its charge while those of the same sign as G go to E and give it the charge that is indicated by the electrometer. The gas loses its conductivity in passing through the tube because it loses its ions.

It should be noted that the charges given to G in these experiments were large. In fact if the tube was held near to a conductor there was an audible discharge from its outer surface. On this account the greatest care had to be taken to prevent leakage. The effect of the charges obtained by diffusion, described previously, was comparatively so small as to be negligible. In the last experiment certain induced charges had to be guarded against and taken into account, into the details of which it is not thought necessary to enter.

13. Summary. — Roentgenized air which has been blown through tubes or rolls of metal foil is charged positively, so long as it retains any conductivity at all. The same tube or roll of metal foil through which Roentgenized air is being blown may receive a positive or a negative charge, depending upon the velocity of the stream of air. Under proper conditions the first part of a tube may receive a negative charge while the more distant part of the same tube receives a positive charge. When moist carbonic acid is used the charges developed in the gas and on the metal are the opposite to those obtained under like conditions with dry or moist air or dry carbonic acid.

A general explanation for all of these results is found in ascribing their cause to the unequal velocities of diffusion of the two kinds of ions in the gas. Villari's hypothesis that the rubbing of the Roentgenized gas against a surface produces a separation of the two electricities, of which either may appear on the metal depending

upon the amount of friction, is not sufficient to explain all of the facts and is therefore untenable.

When Roentgenized air is blown through an ebonite tube having a static charge on its inner surface, this charge is eventually all carried by the ions to the nearest conductor of large capacity against the gas stream.

Villari's assumption that in such a case the charge vanishes, and that in general when Roentgenized air is changed into ordinary air this is done at the expense of an electric charge, is not upheld.

Physical Laboratory, University of Minnesota.



# ON THE RADIANT EFFICIENCY OF THE NERNST LAMP.

BY L. R. INGERSOLI..

A LTHOUGH many tests of the commercial efficiency of the Nernst lamp have been made, there seems to be little available data as to its absolute luminous efficiency, besides the statement in Drude's *Lehrbuch der Optik*<sup>1</sup> placing it at 12 per cent. The object of the present work, therefore, was a determination of the efficiency of the Nernst glower under varying conditions, and an estimate of its temperature from the results. Incidentally, also, it was hoped that the work would give an indication of the accuracy which might be expected of the method employed, which was, in its essentials, the comparatively new one due to Ångstrom<sup>3</sup> and used by him in connection with his determination of the mechanical equivalent of the unit of light.

It is a fact of only too common observation, that different observers, in determining the efficiency of the same kind of light source, arrive at very different results. The discrepancy is doubtless due only to difference in the methods employed, but is of such magnitude as cause one to question results obtained in almost any of the older ways. Each of the two well-known methods of determining efficiency is open to objection. That of using a cell of absorbent solution to free the light from infra-red rays is now generally accepted as unreliable, and, as shown by E. L. Nichols,<sup>3</sup> may lead to widely varying results. That employed by Langley and others, of integrating the energy curves obtained with a bolometer, is unnecessarily complicated when one wishes merely the ratio of the total and visible radiations. Furthermore, strong selective

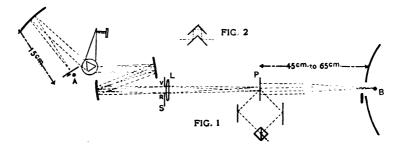
<sup>&</sup>lt;sup>1</sup> Drude, Lehrbuch der Optik, p. 447.

<sup>&</sup>lt;sup>2</sup>Astrophys. Jour., XV., 223. April 1902.

Paper before the A. A. A. S., Washington, 1902. Also PHYS. REV., 17, p. 267.

absorption in the infra-red by different elements of the apparatus renders it sometimes difficult of application.

Ångstrom's method, however, is comparatively free from the above objections and is moreover susceptible of corrections for selective absorption and reflection which are simple and easy of application. In brief the scheme is to disperse the light and screen off all but the visible portion of the spectrum. This part is again combined into white light by a cylindrical lens and balanced photometrically against the total radiation from another exactly similar source. The energy of the two radiations can then be compared by replacing the photometer screen with a thermopile or bolometer and observing the galvanometer deflections for each light. The method is peculiarly well adapted to the Nernst lamp as the great brilliancy of the glower makes possible the use of a narrow slit without too great a sacrifice in intensity.



The general arrangement and dimensions of the apparatus may be seen from the diagram. The two glowers A and B were burned freely in air, without heaters, on a 110-volt alternating current. A voltmeter and wattmeter across the terminals of glower B and a rheostat in series with both lamps enabled one to keep the voltage or power consumption constant at any desired value. As a small difference in voltage makes a considerable difference in the brilliancy of a glower, it was necessary to allow for variations in the pressure

S to cut off the infra-red was made by focusing sunlight on the slit and then with the aid of an eyepiece, setting the screen so that its edge just coincided with the A line  $\lambda$ .76  $\mu$  and clamping it there, the final adjustment being completed by rotating the prism with the tangent screw. This way of adjusting has the advantage of enabling one to secure as fine an adjustment, and to work as near the position of minimum deviation, as desirable. A second screen, approximately placed, cut off the ultra-violet also. Just behind the screens was placed the cylindrical lens L of 14 cm. focal length which recombined the visible spectrum into a strip of white light 1 cm. wide and 3 cm. long.

To compare the energy of the two radiations the photometer head was replaced by a Rubens thermopile connected with a small Thomson galvanometer, whose normal sensibility of  $\sigma . 10^{-9}$  could be reduced by inserting resistance to about one fourth of that, when measuring the unobstructed radiation from the lamp *B*. The galvanometer zero was obtained in each case by closing a small shutter in front of the slit or before the second glower *B*.

In many of the first experiments a small water cell was mounted directly in front of the screen S to absorb any stray infra-red rays due to impurity of the spectrum, but as careful tests failed to discover any appreciable impurity, its use was later abandoned.

The Nernst glower A was mounted so as to allow of adjustment parallel to the slit and was fastened at its ends to prevent its being warped out of position by heating. Glower B was mounted on a carriage sliding on an optical bench about a meter long, and was partly surrounded by a covering with a small opening facing the photometer screen. The photometer head — a type of Lummer-Brodhun — also mounted on the optical bench, was fixed at one position, the photometric balance being made by moving the lamp B with a lever arm. Successive settings of the latter generally varied by less than 2 per cent. and were made in sets of 18 usually, half with the head reversed, and at three different parts of the strip of white light. The proper direction in which to point the thermopile was found by mounting it on a horizontal divided circle and noting the angle for which the galvanometer deflection was a maximum.

Corrections were made for the following sources of error:

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1. Selective reflection by the three silvered mirrors.

2. Selective absorption by the glass prism and lens, or by the water cell (where used).

3. Inaccuracy in setting of the screen at the A line.

- 4. Non-uniformity of the strip of white light.
- 5. Disturbing effect of the wattmeter across glower B.
- 6. Radiation from the shutters before the lamps.

The general scheme of obtaining a correction was to exaggerate the error and note the effect on the final result. A proportional correction could then be deduced. Thus in testing the effect of selective reflection at the three silvered mirrors, a set of four plane silver surfaces (Fig. 2) was mounted just behind the cylindrical lens. The effect of the four additional reflections was to increase the observed efficiency by nearly 7 per cent. of its value (an actual increase of 0.28 per cent. for an efficiency of 4.2 per cent.). The proportional correction of 5 per cent. for the three mirror surfaces is in good agreement with a theoretical correction of 4 per cent. which was roughly calculated from data on the reflecting power of silver for various wave-lengths, given by Hagen and Rubens.<sup>1</sup>

In the same way, by introducing an extra thickness of glass in the path of the luminous radiation, the correction for the selective absorption by the prism and lens was found to be negligible. The effect of the water cell, when used, was also allowed for, the correction being slightly less than that for silver, and opposite in sign. It is evident of course that general absorption, which is non-selective in character, cannot introduce any error.

The accuracy with which the screen to cut off the infra-red could be set at the A line was estimated at about the width of the line itself. This would lead to an uncertainty of about 3 per cent. of the result — the neighborhood of the A line being of course the most effective part of the visible spectrum as regards energy.

the probable error from this source is something less than 2 per cent.

The uniformity of the strip of white light formed by the cylindrical lens was tested photometrically at twenty different points of the area occupied by the thermopile. Diminishing intensity at the ends tended to make the efficiency readings too small and required a correction of 2.5 per cent. (actually 0.10 per cent. for an efficiency of 4 per cent.).

The effect of the measuring instruments connected with glower B was to run this lamp at a slightly lower voltage than the other and hence destroy the perfect similarity of sources presupposed by this method. Tests made by connecting proportional resistances across glower A showed that the effect of this source of error was to lower the observed efficiency 2.5 per cent. Radiation from the shutters and consequent displacement of the galvanometer zero required a correction of something less than I per cent. Proportionality corrections were applied to all galvanometer readings. In no case, however, did the sum of all corrections amount to more than 10 per cent. of the result.

The experiments indicate that the principal factors in determining the efficiency of any glower are its age and the power it consumes. A table with some typical results is given on the following page.

Glowers are by no means uniform. New glowers show an efficiency of from 4.35 per cent. ( $\pm$ .10 per cent.) to 4.70 per cent. ( $\pm$ .10 per cent.)—mean 4.61 per cent. The efficiency falls rapidly for about the first twenty hours, decreasing to 4.3 per cent. and varies only slowly after this. Tests on glowers of 40 hours age and upwards gave efficiencies of from 3.9 per cent. to 4.4 per cent.—mean 4.17 per cent. Some very old glowers gave results of only 3.6 per cent. It is noticeable that after a glower has been burned upwards of twenty hours it develops a marked crystalline appearance and it is probable that the fall in efficiency is due to the greater radiating surface and consequent lower temperature afforded by the crystalline structure.

The above figures are all for 110-volt glowers furnished by the Nernst Lamp Company, of Pittsburg, and consuming 89 watts power. For every watt above 89 within narrow limits the efficiency increases

Age of Glower.	Power Consumed.	Observed Efficiency.	Total Correction.	Corrected Efficiency.
New.		4.85 %	—. <b>15</b> %	4.70 %
"	89 ''	4.61	.00	4.61
5 hours.	89 ''	4.23	+.13	4.36
New.	88 ''	4.44	09	4.35
18 hours.	88 ''	4.15	10	4.05
42 ''	88 ''	4.10	09	4.01
New.	91 ''	4.84	17	4.67
8 hours.	90 ''	4.67	11	4.56
21 ''	90.5 ''	4.48	14	4.34
Over 40 hours.	89 ''	4.05	· .23	4.28
	** **	4.02	.23	4.25
** ** **		4.03	.23	4.26
** ** **	** **	3.99	• .23	4.22
** ** **	** **	4.06	• .24	4.30
** ** **	** **	3.89	+ .17	4.06
** ** **	** **	4.10	16	4.26
** ** **	** **	3.85	+.16	4.01
** ** **	** **	3.80	· .30	4.10
** ** **	** **	3.93	04	3.89
** ** **	** **	4.20	05	4.15
Very old.		3.63	05	3.58
	•• ••	3.63	01	3.62

0.06 per cent., and below, vice versa. In the above table the correction contains a reduction to this uniform condition.

The energy curve plotted from Wien's law which gives the efficiency 4.17 per cent., *i. e.*, which gives the ratio visible energy / total energy = .0417, is that corresponding to the temperature  $2,360^{\circ}$  C. absolute. This then would be the temperature of the Nernst glower considering it as a black body. It will be noted that it lies well within the limits, 2,200° to 2,450°, given by Lummer and Pringsheim,<sup>1</sup> their estimate being based on the position of  $\lambda$  max in the energy curve.

Another check on the above work as well as an indication of the extent to which the Nernst glower follows the laws of a black body is afforded by noting the increase of efficiency with power consumed. If we assume a temperature of 2,360° C. for an ordinary 110-volt glower taking 89 watts with an efficiency of 4.17 per cent., the same glower taking 95 watts, will have an efficiency of 4.53 per cent. indicating a rise in temperature of about 40 degrees. Now if the

<sup>1</sup> Verh. deutsche Phys. Ges., 190, 13, p 36-46.

glower acts as a black body the total radiation will vary as the fourth power of the temperature, or the ratio of the two radiations will be  $2,400^4/2,360^4 = 1.069$ . In reality this ratio will be very approximately 95/89 = 1.067, supposing the convection and other losses to be a constant fraction of the whole. Of course the closeness of this agreement is only accidental, the probable error being much greater than the difference between these figures.

I wish to acknowledge my indebtedness to Prof. C. E. Mendenhall and Prof. Snow, of the physics department, for material assistance as well as many valuable suggestions in connection with this work.<sup>1</sup>

PHYSICAL LABORATORY, UNIVERSITY OF WISCONSIN, July 21, 1903.

<sup>1</sup> Mr. L. W. Hartman in a recent paper on the luminous radiation from the Nernst glower (PHYS. REV., 17, p. 65), which has appeared since the above was written, notes that old glowers seem to show an increase in light intensity instead of a decrease as the above work would indicate. The discrepancy is probably due to the fact that his results were obtained while keeping the current rather than the power consumption, constant. As the resistance of a glower increases with age a constant current means an increase of power consumption and hence a greater emission.

Mr. Marshall Hanks of the Nernst Lamp Co. informs me that the commercial efficiency curves show a characteristic drop, but that an effort is at present being made to age the glowers before sending them out, hence future tests may not show this effect.

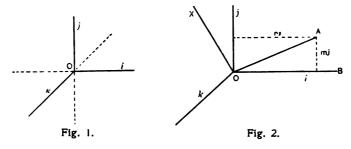
## QUATERNIONS IN ELECTRICAL CALCULATIONS.

BY OLIN J. FERGUSON.

#### PRELIMINARY.

MAXWELL, in his works, uses quaternions in their most general form. This paper is intended to analyze the quaternion in two special cases, and for the benefit of electrical students who are not acquainted with this form of expression a few preparatory remarks are given.

Conceive of three operators  $i, j, k, \perp$  each to each (see Fig. 1). Let the operation of any one of these upon another signify the revo-



lution of the one operated upon through a right angle toward the left of the observer when he is standing upon the operator, looking toward the one operated upon.

That is,

ij = k; jk = i; ki = j; ji = -k; kj = -i; ik = -j. i(ij) = -j, or  $i^2 = -1$ .

Therefore, Similarly,

 $k^2 = j^2 = i^2 = -1.$ 

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multiple of *i*. For example, ai, bi, etc. Making the same assumption for j and k, we see that a vector in the plane of the ij-axis may be expressed by the sum of *i*- and *j*-vectors (see Fig. 2).

$$OA = ni + mj$$

or, if OA is of length a units,

$$OA = (a \cos AOB)i + (a \sin AOB)j.$$

In general, any vector through O, say OX of length x units, will be expressed by

$$OX = (x \cos \beta)i + (x \cos \gamma)j + (x \cos \delta) k,$$

where  $\beta$ ,  $\gamma$ ,  $\delta$  are the angles between OX and the *i*-, *j*-, *k*-axes respectively.

We will now assume that any real quantity when acted upon by i will be revolved to lie along the *i*-axis. Then iA is a vector along the *i*-axis. Therefore,

$$iA = ai$$
.

But from previous conditions,

$$i(iA) = -A.$$

That is, two operations by *i* revolves A through 180°, or each operation revolves it through 90°. Therefore, A is perpendicular to *i*. Similarly, A is perpendicular to both *j* and *k*, and we have four axes at right angles each to each. A vector having for its components certain projections upon each of these four axes will have the length expressed by the square root of the sum of the squares of these resolved parts.

As for terminology, a real part of a quantity is called a "scalar," and is measured along the real axis. The length of a vector is its "tensor," and is expressed TX (read "tensor of X").

## IMPEDANCE.

Z = impedance.

Assume a vector E, of length e (that is, TE = e), rotating in the plane ij with the angular velocity  $\omega$ . Let t represent the time elapsed since the start from the *i*-axis. The equation to represent this vector is,

OLIN J. FERGUSON.

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$$E = e (i \cos \omega t + j \sin \omega t).$$

The part  $i \cos \omega t + j \sin \omega t$  is called the "versor."

Let E represent a harmonically varying E.M.F. Let, also,

$$I = i (i \cos \omega t - \theta + j \sin \omega t - \theta)$$

represent the resulting current, with a difference of phase  $\theta$ .

$$TI = i.$$
$$E = ZI$$

By definition,  $E_i I$  is the operator which, acting upon I, will produce E.

Therefore,

$$(E/I)I = E = ZI.$$
$$E/I = Z.$$

But,

$$I = i (i \cos \omega t - \theta + j \sin \omega t - \theta).$$

Multiply the above value of / by the assumed quantity,

$$\frac{\mathrm{e}}{\mathrm{i}}(\cos\,\theta+k\,\sin\,\theta),$$

and we will get

$$e (i \cos \omega t - \theta \cos \theta + j \sin \omega t - \theta \cos \theta$$

+ 
$$ki \sin \theta \cos \omega t - \theta + kj \sin \theta \sin \omega t - \theta$$

This reduces to

$$e (i \cos \omega t - \theta \cos \theta - i \sin \omega t - \theta \sin \theta$$

$$+ j \sin \theta \cos \omega t - \theta + j \cos \theta \sin \omega t - \theta$$

which equals

$$e (i \cos \omega t + j \sin \omega t) = E.$$

Therefore,

$$EI = Z = \frac{e}{i}(\cos \theta + k \sin \theta).$$

This kind of a quantity is called a quaternion and consists of

be looked upon as the sum of a scalar,  $\frac{e}{i} \cos \theta$ , and a vector,  $\frac{e}{i} k \sin \theta$ .

These parts have the following interpretation :

Scalar part = 
$$\frac{e}{i} \cos \theta = r$$
.  
Vector part =  $k \frac{e}{i} \sin \theta = kx$ .  
Tensor part =  $\frac{e}{i} = z$ .

Versor part =  $\cos \theta + k \sin \theta = k^{\pi/2} = k^{\pi}$ .

The quantities, r, x, z, have the ordinary interpretation and

 $z = \sqrt{[r^2 + (\omega L - I/\omega C)^2]}.$ 

The versor is the "turning" operator.  $\cos \theta + k \sin \theta$  turns *I* through the angle  $\theta$  and is therefore only a part of k, which would turn it through one right angle. The relation between the two is expressed above.

POWER.

$$E = e(i \cos \omega t + j \sin \omega t).$$
  

$$I = i(i \cos \omega t - \theta + j \sin \omega t - \overline{\theta}).$$
  

$$EI = power = P.$$

 $P = ei(t^2 \cos \omega t \cos \omega t - \theta + ij \sin \omega t \cos \omega t - \theta +$ 

$$ji \cos \omega t \sin \omega t - \theta + j^2 \sin \omega t \sin \omega t - \theta$$
.

 $= ei(-\cos \omega t \cos \omega t - \theta - \sin \omega t \sin \omega t - \theta +$ 

$$k \sin \omega t \cos \omega t - \theta - k \sin \omega t - \theta \cos \omega t$$

 $= \operatorname{ei}(-\cos\theta + k\sin\theta).$ 

Whence, P is also a quaternion (see Z).

Scalar part =  $-ei \cos \theta = -real power$ . Vector part =  $kei \sin \theta$  = imaginary power. Tensor part = ei = TEI. Versor part =  $-\cos \theta + k \sin \theta$ .

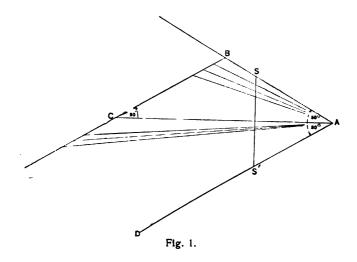
The imaginary power is at right angles to the real power and is not what we call the wattless power. The latter is  $ei(1 - \cos \theta)$  while the former is  $ei \sqrt{(1 - \cos^2 \theta)}$ .

UNIVERSITY OF NEBRASKA.

## A CONSTRUCTION FOR DIRECT-READING SCALES FOR THE SLIDE WIRE BRIDGE.

BY EDGAR BUCKINGHAM.

WHEN a large number of rough measurements are to be made on the slide wire Wheatstone's bridge, it is very convenient to have the scale so divided as to read, directly, the ratio of the two segments of the wire, thus obviating the necessity of working out the ratio  $\alpha/(1,000 - \alpha)$  or looking it up in Obach's table. Such scales are, of course, in common use, but until a few days ago I have never considered how they might be made by a simple geometrical construction. The following method will accomplish the



desired result; it may very possibly be familiar, but I do not remember seeing it given.

Suppose we have at our disposal some scale of equal parts, such as a meter stick. Construct an isosceles triangle ABC having the equal sides BA and BC each 1 m. long, and the equal angles

No. 5.]

C, be laid off in equal parts (the divisions of the meter stick, for example). Lines drawn from the points thus obtained to the vertex A, will divide in the desired manner any line SS' perpendicular to AC and limited by AB or its continuation, and a line AD drawn symmetrically with AB at an angle of  $30^{\circ}$  on the other side of AC. Any scale which it is desired to divide may be made to occupy the position SS', and may then be divided at once by the use of a straight edge and a pin at A.

If, for example, the side BC be divided into one hundred equal parts, the successive divisions of SS', beginning at S and numbering them 0.01, 0.02, 0.03, etc., will give the ratio of the length of that part of the scale on the side toward S to the length of the other part on the side toward S'.

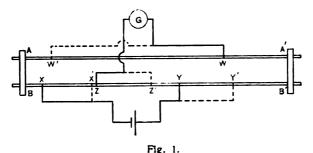
BUREAU OF SOILS, WASHINGTON, D. C., July 14, 1903.

# A METHOD FOR THE COMPARISON OF LOW RESISTANCES.

#### BY FRANK WENNER.

THE Wheatstone's bridge furnishes our best means for the comparison of resistances but with low resistances certain wellknown difficulties arise. Ways have been devised for overcoming these difficulties yet it is believed that the following method has advantages not possessed by the others so it is presented with the hope that it will be of service to some one.

Referring to the diagram let AA' and BB' be the conductors whose resistances are to be compared. These are joined by conductors AB and A'B'. Two points X and Y on BB' are connected to the terminals of the battery. The galvanometer is connected to a point Z between X and Y and a point W on AA' such that the bridge is in balance. Move the connections X, Y and Z in



the same direction through equal resistances to points X', Y' and Z'. To again balance the bridge the connection W must be moved to a point W' such that the resistance of AA' between W and W' is equal to the resistance of BB' between X and X', Z and Z' or Y and Y'.

The statement hardly needs a proof for it is easily seen that the resistance in each of the four arms of the bridge is increased and decreased by the same amount.

DEPARTMENT OF PHYSICS AND ELECTRICAL ENGINEERING, IOWA STATE COLLEGE, August, 1903.





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JOSIAH WILLARD GIBBS



Number 6.

### THE

# PHYSICAL REVIEW.

## ON THE MAGNETIC EFFECT OF ELECTRIC CONVECTION.

By VICTOR CREMIEU AND HAROLD PENDER.<sup>1</sup>

DETAILED discussion of the present state of the question of electric convection has been recently given in an article by Cremieu in the December number of the Journal de Physique. Contradictory results have been obtained, some seeming to prove the existence of a magnetic field around a moving charged body, others seeming to prove the non-existence of such an effect.

In the same article the conditions necessary for a proper experiment on electric convection have been clearly set forth. We shall recall that the realization of the following conditions is imperative :

1. That the charge is actually carried along - entraince - by the body in motion.

2. That only this charge can act upon the apparatus destined to detect the magnetic affect attributed to its entrainement.

3. That, during its entrainement, the charge undergoes no variation; in particular, that the loss by leakage is limited to a very small fraction of the total charge carried.

In the hope of reconciling the contradictory results obtained by the various experimenters on this question of fundamental importance, M. H. Poincaré took the initiative in the fall of 1002 to Later a later a set in the second second of the second second

accordance with the suggestion of Lord Kelvin, Paris was chosen as the most favorable place for these joint experiments, and M. E. Bouty gladly put at the disposal of the two investigators his laboratory at the Sorbonne.

Accordingly, invited by Messrs. Poincaré and Bouty in the name of the University of Paris, Mr. H. Pender, whose experiments have invariably given positive results, went to Paris in January, 1903, to work in collaboration with M. V. Cremieu, whose experiments have always been of a negative character. The Johns Hopkins University put at Pender's disposal all the apparatus necessary, and obtained from the Carnegie Institution the funds necessary to defray the expenses of the journey. The expenses of the actual experimenting were met by the Institut de France.

We wish here to express to M. H. Poincaré and to M. E. Bouty our gratitude for their initiative and liberality. Through their invaluable aid in advice and criticism, we have been able to realize in three months an almost complete program of very delicate experiments. Thanks to the most excellent organization of the laboratory of M. Bouty, we have not once been delayed by lack of apparatus or of any physical means whatever.

Also it gives us great pleasure to express our gratitude for the liberalities of the Carnegie Institution, of the Johns Hopkins University, and of the Institut de France.

Repetition of Pender's Experiments.— Cremieu in 1899–1900,<sup>1</sup> was led to repeat Rowland's experiment, and, for considerations elsewhere developed, he modified considerably the method. Instead of the direct magnetic effect, he studied the electromagnetic induction of a moving charged body. The experiment gave negative results, which persisted during a long series of observations, in spite of many modifications of details suggested by objections from numerous sources.

At the suggestion of Rowland, Pender took up the method of Cremicu, improving it in some details. His experiments were first carried on in the Physical Laboratory of the Johns Hopkins University and later in the country free from the disturbances of any ELECTRIC CONVECTION.

have been published elsewhere.<sup>1</sup> The results were invariably positive, and in the second series the observed and calculated values accorded within less than 5 per cent.

Pender brought with him to Paris all his apparatus, which we at once set up under conditions as nearly similar as possible to the original disposition. The only condition we were unable to realize was the same degree of mechanic and magnetic stability. Nevertheless, we were able to find again the qualitative effects of magnetic induction already observed by Pender. We verified with a sufficient degree of approximation the proportionality of these effects with the speed of rotation of the discs and with the surface density of the charge carried around. We also found that the effects of the two discs were superimposed or annulled each the other, according to their relative directions of rotation, and that the effect obeyed the law of the distance between the discs and the induced coil. As to the order of magnitude of the quantities observed, the deflections obtained varied from 58 to 800 mm., according to the values of the other quantities involved, on a scale placed 4 meters from the galvanometer.

Repetition of Cremieu's Experiment. — Cremieu in the meantime mounted his induction experiment, the conditions being almost identical with those of the original experiment. However, the galvanometer previously employed had been destroyed, so we were obliged to use another. Also the conditions of stability were not so good as in the original installation.

Although the effects due to charging and discharging the disc at rest were not entirely eliminated, we obtained with a sufficient degree of certainty the same negative results as in the original experiment.

Verifications in Cremieu's Experiment. — In these two experiments we employed continuous metal discs turning between continuous parallel condensing plates. In the course of the repetition of Pender's experiment we observed the following fact. When a voltage was employed sufficiently high to cause sparks to spring across from the discs to the condensing plates, the magnetic effect observed

<sup>1</sup> Phil. Mag., 6th series, Vol. 2, p. 169, 1901 et loc. cit., PHYS. REV., Vol. XV., p. 291, 1902, et loc. cit.

fell practically to zero, whereas the potential of the discs, as measured by an electrometer connected thereto, showed a decrease of less than a tenth of the value observed just before the sparks began. In Cremieu's apparatus it was impossible to see such sparks if they should occur, as the disc turned in a completely closed box of cast iron. However, in spite of the fact that the disc and condensing plates were covered with a thin layer of caoutchouc, it was possible that such sparks might occur, as the distance between these pieces was very small.

Only a galvanometric measurement of the quantity of electricity taken by the disc at each charge or the quantity given up at each discharge could decide this point. We made this measurement, employing voltages from 1,000 to 5,500 volts. For 1,000 volts it is certain that no spark can occur across 3.5 mm. of air. As the voltage is increased, one should obtain currents proportional to the voltage as long as no sparks occur. If such sparks take place, the charging current should increase more rapidly, the discharge current less rapidly, than the voltage. Measurement showed that up to 5,500 volts, the maximum potential employed, there was a strict proportionality between the charge and voltage.

The cause of Cremieu's negative results was not then in this.

Verifications in Pender's Experiments. — In the series of experiments on "open currents" made by Cremieu<sup>1</sup> in 1902 with the aid of M. J. Jarval, certain peculiar magnetic effects were observed in the neighborhood of a node of electrical oscillations such as is formed by the turning disc in convection experiments. The conditions for the production of these effects are sufficiently similar to the conditions in Pender's experiment, that one might believe that the effects observed were due to such oscillations and not to convection itself.

This hypothesis was rendered still more plausible by certain effects observed when the discs are charged or discharged at rest.

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protects the coil. Again, as the tin foil is wrapped around the winding of the coil only, thus leaving the center of the coil open, any electric oscillation through the coil will suffer little damping.

To ascertain if such oscillations played any rôle, we placed Pender's coil in a box of brass with walls 2 mm. thick, entirely closed. This diminished considerably the perturbations caused by charging and discharging the discs at rest, but the magnetic effect due to the movement remained practically of the same order to within 10 per cent., that is, as close as we could observe under the unstable conditions of the experiment.

However, in Cremieu's negative experiments, the iron box in which the disc turns can arrest *every* magnetic oscillation tending to traverse the coil; this box constitutes a perfect magnetic screen, which is not the case with the brass box in which we enclosed Pender's coil. In fact, it is well known that damped electric waves, such as those which occur around a body whose charge is rapidly varying, traverse without considerable alteration even very thick conducting screens. To verify this point, it would therefore have been necessary to put a magnetic screen around Pender's coil.

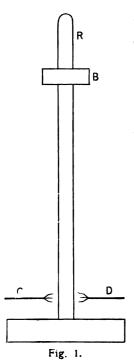
The following method of procedure is, however, much simpler. If the effects observed by Pender are due to an oscillatory phenomenon, they must certainly be modified by any change in the circuits serving to charge and discharge the discs.

We placed in these circuits liquid resistances. They did not cause the effect to disappear; they merely diminished considerably the perturbations at rest.

Again, we placed in parallel with the discs a variable capacity. The capacity of the discs was 200 C.G.S. electrostatic units. The capacity in parallel was an air condenser and could be varied by sixths from 166 to 1,000 C.G.S. This time the effect in motion was considerably diminished. The diminution was approximately proportional to the capacity in parallel with the discs. At the same time we noticed a diminution in the capacity assumed by the discs. (In all our experiments we used as the source of charge M. Bouty's high potential storage battery, capable of giving as much as 14,000 volts.) The potential was measured by an electrometer connected automatically to the discs at the moment they were

charged. However, there was not a proportionality between the diminution of the voltage and the diminution of the deflection. The deflection dropped to one third its original value, whereas the decrease in voltage was only 10 per cent. However, we discovered that the discs no longer became completely discharged, and that the charge remaining on the discs was proportional to the capacity in parallel.

These facts led us to study the duration and number of contacts necessary to charge or discharge a condenser completely. A cylin-



drical rod R, Fig. 1, of ebonite, 120 cm. long, was placed vertically in such a manner that a brass ring B, I cm. high, could fall freely along R. At 10 cm. above the lower end of the rod were placed two metallic brushes C and D, opposite each other. The brass ring B in falling made contact between C and D for any desired interval of time, depending upon the length of the drop. The condenser employed was the same as that put in parallel with the discs. The source of electricity was the high potential storage battery of M. Bouty, the capacity of which can be considered infinite in comparison with that of the condenser.

The experiment was made as follows: First, was measured the potential of one pole of the battery when the other was earthed. One plate of the condenser was connected to earth, the other to the brush D. The brush C could be connected either to the free

pole of the battery or to the earth. First, let C be connected to the battery, and let the ring fall, contact will be established between C and D as the ring passes. The duration of the contact could be varied between  $\frac{1}{D}$  and  $\frac{1}{D}$  of a second. After the fall the potential

1. The potential assumed by the condenser was always inferior to that of the battery. This difference was inversely proportional to the time of contact and directly proportional to the capacity of the condenser.

Next the condenser was charged by a prolonged contact with the battery and then insulated from it, C was connected to the earth, and the ring B dropped. The electrometer connected to the condenser then indicated if the condenser retained a charge after contact. We observed the following :

2. The condenser always retained a residual charge, the value of which was directly proportional to the capacity of the condenser and inversely proportional to the duration of the contact.

However, the difference between the potential of the battery and that taken by the condenser after contact was much greater, all else being the same, than the residual potential after the discharge.

These facts explain satisfactorily the diminution of the effects of induction of the discs in motion when the capacity is put in parallel with the discs. The presence of this capacity decreases the variation of the charge at each reversal of the commutator, and, in consequence, the effects of induction, which are proportional to this variation; further, the indications of the electrometer, which gives the maximum potential assumed by the discs, cannot be affected to the same degree.

Consequently, it appears that the effects observed in Pender's experiment are due to the movement of the charged discs, as demanded by the theory of electric convection.

Verifications Without Fixed Condensing Plates. — To eliminate entirely the questionable rôle of the fixed condensing plates, we made the following modification.

Pender's two discs, diameter 31 cm., were placed opposite each other at 1 cm. apart, and arranged to turn in opposite directions. Concentric with the two discs was placed a coil 34 cm. in diameter and 3 cm. thick. This coil, which was entirely enclosed in a brass sheath, consisted of 1,300 turns of copper wire with a total resistance of 60 ohms. The commutator was arranged so as to connect this coil to the galvanometer synchronously with the charging and discharging of the rotating discs. The deflections of the galvanometer under these conditions was much less than in the former experiments, on account of the considerable decrease in the capacity of the two discs thus arranged. In spite of that, however, the deflection was sufficiently large to be measured, and the agreement between the observed and calculated deflection was quite satisfactory.

Here we stopped our experiments with the induction method. These experiments can, in fact, give no information in regard to the nature of the magnetic field produced by the movement of the discs, whereas it is essential to know if this field is permanent with the rotation, or is merely an instantaneous field produced at the moment of charging or reversing the charge, resulting from magnetic perturbations thereby set up.

Experiments on the Direct Magnetic Effect. - First we utilized the same arrangement as in the preceding induction experiment. The coil was replaced by a delicate astatic system enclosed in a metallic tube so arranged that the lower needle of the system was I cm. above the upper edge of the discs, in a plane equally distant from the two. The tube was protected from the air currents caused by the rotating discs by a large sheet of mica properly placed. The sensibility of the system was determined by a test coil, of a radius equal to the mean effective radius of the disc. The reversal of a current of 10<sup>-4</sup> ampères in this coil gave a deflection of 20 mm. on a scale 4 meters distant. The convection current possible to realize in this disposition was only  $2.5 \times 10^{-5}$  ampères, and in consequence the deflection expected was scarcely 5 mm. Hence the experiment was purely quantitative. However, there was no doubt as to the effect. At each reversal of the sign of charge on the turning discs, the system was deflected in the expected direction, but it was impossible to say, on account of the unsteadiness of the needle, whether the deflection was permanent or only an impulse.

It is to be noted that in spite of the smallness of this result, it is nevertheless of great importance. Any perturbing effects due to the fixed condensing plates or to currents which might circulate in the moving discs, are entirely eliminated, because the first are suppressed, and the second would destroy each other, as the discs turn in opposite directions.

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In the above experiment, only a very small part of the discs is effective. The needle is in a very unfavorable position, for the magnetic field over the edge of the discs is very unstable, and further the needle is very poorly protected against the air currents, which cause considerable unsteadiness. These considerations led us to return to Rowland's original method.

A single disc turning in a horizontal plane was enclosed in a box of ebonite, the inside of which, covered with tin foil, formed the condensing plates, thus increasing considerably the capacity of the disc. This arrangement allowed us to put the astatic system very close to the disc, in a region where the magnetic field is at the same time horizontal and quite constant; and finally, the effects of the air currents were entirely eliminated. We were therefore enabled to give the needle a much longer period, without having to fear so much the mechanical perturbations which might be produced during the time necessary for the system to complete its swing.

This time the deflections obtained were considerable, 20 to 30 mm., of the order and in the direction expected. But it was still impossible to decide with certainty whether the deflections were permanent or simply impulses.

Pender observed in his former experiments,<sup>1</sup> in which a perfect stability was realized, deflections which were undoubtedly permanent, but he did not know at that time of the magnetic effects which are produced in the neighborhood of nodes of electric oscillations such as formed by the discs, a description of which Cremieu has recently given.<sup>2</sup> He was therefore not absolutely certain that the deflections he observed were not due to such oscillations, the effects of which might be easily confused with those due to a permanent magnetic field presumably due to the convection current.

These considerations led us to modify both our mode of operation and the system used to detect the magnetic field.

*New Mode of Operation.* — In all the experiments performed up to the present by other experimenters and ourselves, the effect observed was always that resulting from charging or reversing the sign of the charge on the discs already in rotation. Of course, care

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<sup>&</sup>lt;sup>1</sup> PHYS. REV., Vol. XV., Nov., 1902; Phil. Mag., Vol. V., Jan., 1903, p. 34. <sup>2</sup> C. R., Vol. CXXXV., p. 153, 1902.

was always taken that there was never an effect produced by charging or reserving the charge on the discs at rest, which condition can be realized by properly enclosing the astatic system (or galvanometer circuit) in a suitable conducting screen. However, the action of such a screen is both electrostatic and electromagnetic. Besides. it is well known that in the neighborhood of a node of electric oscillations there are produced rapidly damped magnetic waves capable of demagnetizing a magnet; and such a demagnetization can result in a permanent change of the position of equilibrium of an astatic system. Moreover, it is unknown what effect the movement of the body forming the node for these oscillations can have upon the oscillations themselves. Consequently one cannot assume a priori that a screen which is sufficient to suppress any effect of these oscillations when the discs are at rest will also be sufficient when the discs are in motion.

The following mode of operation appears to us to avoid all these inconveniences. First, charge the disc at rest, care being taken that this operation produces no effect on the magnetic system. Then insulate the disc from the charging source and set it in motion. The magnetic system should then, if the effect of convection exists, take a deflection increasing with the velocity, permanent for any given velocity, and returning to zero the moment the disc is stopped. An electrometric measurement of the potential of the disc before and after the movement will show if there has been any sensible leakage.

As ordinary astatic systems are poorly suited for such an experiment, we attempt to construct a system of a different kind.

Experiments with New Magnetic Systems. — It is difficult to realize, in most laboratories, a magnetic stability sufficient to allow of the measurement of magnetic fields as low as  $10^{-6}$  C.G.S. electromagnetic units, the order of the field in most convection experiments. Further, from the very nature of its construction, a sensitive astatic system always tends to drift in a certain definite direction, due to the slow and unequal demagnetization of the needles which compose it. Another cause of instability is that the direction assumed by such a system is determined by the difference between the earths'

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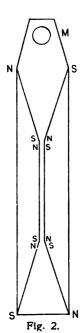
variation in either of these fields will produce a considerable change in the position of equilibrium of the system. In particular, if the field to be studied is produced by oscillatory phenomena more or less damped, astatic systems become practically useless, since the demagnetizations which accompany these damped oscillations not only affect the system itself but also the directing magnets. Finally, in the case where the field to be studied is very feeble, it seems advantageous to increase the effect by using strong magnetic poles, but it is well known that the sensibility of an astatic system is independent of the moments of the magnets which form it.

All these inconveniences can be avoided, without decreasing the sensibility, by employing an extremely simple system. This system consists essentially of a light horizontal beam carrying at one end a vertical magnet, and at the other a non-magnetic counter-weight of brass. The whole is supported by a long, fine metallic wire fixed to the center of the beam. If the magnetic axis of the magnet is exactly vertical, the couple to which this magnet is submitted due to the earth's field will produce no action on the torsion wire. The beam will therefore take up a position due only to the torsion of the wire which supports it. To adjust the system to this condition, the magnet is first replaced by a non-magnetic needle of the same form and weight, and the period of oscillation of the system is determined. The magnet is then replaced. In general the period of oscillation becomes much shorter and the beam takes up a new position of equilibrium. However, by adjusting the counterweight, an exact verticality of the magnetic axis of the magnet can soon be attained, which is indicated by the system again taking the same period of oscillation as when the magnet was replaced by the nonmagnetic needle. A magnetic system is then realized which is directed only by the torsion of the supporting wire.

With systems of this kind we have obtained very great sensibilities. For example, for a magnetic pole of 20 C.G.S., supported by a silver wire 95 cm. long and .025 mm. in diameter, we obtained a deflection of 34 mm. on a scale 2 meters distant, for a variation of field of  $10^{-6}$  C.G.S.; the period of oscillation being about 60 seconds. When this system was placed near the disc in a suitable screen, it was absolutely unaffected by the starting of the motor and the discs.

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However, an unexpected effect prevented us from obtaining what we had hoped. At the end of about two minutes of rotation of the disc, over which the system was placed, the system began slowly to • deflect, the deflection increasing as time went on, thus rendering all observations impossible. At first we attributed these deflections to air currents set up in the screen containing the system by the heating of the condensing plate over the disc. This plate became quite warm on account of the violent vibrations caused by the rapid motion of the disc. But the "dummy" system, with the nonmagnetic needle gave no such deflections; hence the effect could not be attributed to air currents. We finally concluded that the cause of this effect was the following : The rotation of the disc im-



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mediately below the pole of the magnet causes Foucault currents to be set up in the gilded surface, and the reaction of these on the magnet produces either a slow demagnetization or a change in the position of the magnetic axis of the needle with respect to its geometric axis. But be the cause what it may, we were forced to abandon the use of such systems.

Returning then to the ordinary systems, we constructed a very simple one in the following manner. Three pair of very fine steel needles magnetized to saturation were arranged upon a thin sheet of mica as indicated in Fig. 2. This system was 6 cm. long and weighed about 500 mg. It was suspended inside a metallic tube from a silk fiber about a meter long. A test current sheet, constructed in such a manner as to give a distribution of current similar to that which is produced by the turning disc, was used to determine the sensibility of the system. When this test sheet was put in place of the disc and a current of

10<sup>-4</sup> ampères reversed through it, the system was deflected 120 mm. This sensibility was amply sufficient, since the convection

which we employed are magnetic, and very unequally so at different points. Consequently the system would take different positions

ent points. Consequently the system would take different positions of equilibrium depending upon the part of the disc immediately under it. However, if the disc is given a velocity such that it makes at least one complete turn during the time required for a complete oscillation of the system, the latter will take a mean position of equilibrium, which will not change when the velocity is augmented.

We therefore proceeded as follows: The disc was given a slow rotation, the equilibrium position of the system noted, the disc then charged, and the position of equilibrium again noted. Thanks to the liquid resistance in the charging circuit, the change in the equilibrium position was too small, if any, to notice. Then the speed of rotation was increased to its maximum, maintained at such for some time, and the position of equilibrium again noted; finally, the velocity was reduced to its first value and another reading taken.

In this way we assured ourselves of the following.

There was a deflection of the system when the velocity was increased, in the direction demanded by the theory of electric convection.

The deflection was permanent.

It accorded quantitatively to 10 or 20 per cent. with the calculated deflection.

From all the foregoing results, corroborated by those previously obtained by Pender, we can conclude that,

A charged disc, having a continuous metallic surface, turning in its own plane between two fixed condensing plates, parallel to this plane, produces a magnetic field in the direction and of the order required by the theory of electric convection.

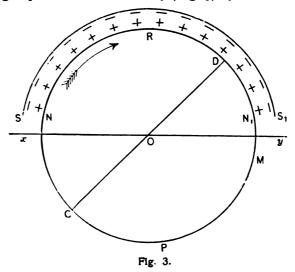
There now remained two questions for us to solve.

I. Are the magnetic effects thus obtained due to an actual *entrainement* of the charge by the moving metallic surfaces, or can they be attributed in any way to conduction currents, open or closed, produced by the relative movement of the disc and the condensing plates?

2. What cause concealed from Cremieu the effects observed by Pender in his previous experiments and also observed by us in common in the experiments just described ?

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Experiments on the Entrainement of the Charge by Continuous Metallic Surfaces. — To answer the first question we first undertook an experiment the idea of which is due to Hertz and the first attempt at realization to Rowland. Consider a plane ring, continuous and conducting, represented schematically (Fig. 3) by the circle NRMP.



This ring can turn in the direction of the arrow under a fixed condensing plate represented by the arc  $SS_{1}$ , covering only a portion of the moving ring. Let the arc covered by this condensing plate be I/nth of the whole circumference, let  $\rho$  be the distance between the planes of the two plates NRMP and SS<sub>1</sub>,  $\gamma$  the linear velocity of any point on the ring NRMP. Suppose SS<sub>1</sub> charged to a negative potential K, and NRMP connected permanently to the earth. As each element ds of NR MP arrives opposite S it will become charged by influence. If the hypothesis ordinarily assumed is true, this element should carry its charge along with it. In other words, this charge will be displaced with reference to the electrostatic field between NRMP and SS<sub>1</sub>, which remains fixed in space. When ds arrives opposite  $S_1$ , the charge on it is no longer retained by influence. As this is true for all elements of NRMP there will result from the movement a constant difference of potential between the two points N and  $N_1$  on the moving ring opposite S and  $S_1$ ; consequently conduction currents will be set up in the ring, and



will be distributed according to the relative resistances of the sectors  $NRN_1$  and  $NPN_1$ .

A magnet placed above R will therefore be subjected to magnetic field due to two causes, first, that due to a convection current in the direction of the arrow, second, that due to a conduction current in the opposite direction. If the needle is placed over P it will be acted upon by the conduction current only. Moreover, the sum of the conduction currents in NRN, and NPN, should be equal to the intensity i of the convection current.

Let  $\sigma$  be the surface density of the charge on  $NRMP_1$  then the intensity of the convection current due to a ring I cm. wide is

 $i = \sigma_{\gamma}$ .

But

$$\sigma = \frac{K}{4\pi\rho}$$

Hence

Let R be the total ohmic resistance of the conducting ring.  
Then the resistance of 
$$NRN_1$$
 is  $R/n$  and that of  $NPN_1$  is  $R(n-1)/n$ . The conduction current in  $N_1RN$  is then evidently

$$-i_1 = -i\left(\frac{n-1}{n}\right)$$

The magnetic field at a distance above R great with respect to  $\rho$ will be due to the difference between i and  $i_1$ , that is to

$$i\left(1-\frac{n-1}{n}\right)=+\frac{i}{n}$$

Similar reasoning shows that the field over P is proportional to -i/n.

Hence a magnetic system placed over P or over R will show magnetic effects equal and in opposite directions.

$$\sigma = \frac{K}{4\pi\rho}.$$

 $4\pi\rho$ 

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thin gold leaf on an ebonite disc, the width of the ring being 5 cm. and the mean radius 14.5 cm. The ring was divided by concentric scratches into strips 1 cm. wide. The calculated intensity of the convection current was  $4 \times 10^{-3}$  ampères. The deflections of an astatic system placed over P were in the direction expected and accorded quantitatively with the calculated values within the usual approximation in our experiments, *i. c.*, 10 to 15 per cent.

However, by slightly modifying the experiment, we were able to measure the quantity of charge carried around with great precision. If the two points on the disc immediately under S and  $S_1$  are connected to a galvanometer the resistance of which is of the same order as the halfs of the ring NRMP, there will flow through the galvanometer a current easily measureable, since it will be a considerable fraction of the convection current, that is to say, in this experiment, of the order of  $10^{-5}$  ampères. The gilding on the disc can be made extremely thin, having a resistance of from 4 to 6 ohms per square centimeter of surface. The resistance of one half the ring on our disc was 6 ohms. We employed a galvanometer of the D'Arsonval type (Hartman and Braun) having a resistance of 4.38 ohms and sensitive to 10<sup>-7</sup> ampères. Hence for a convection current of  $4 \times 10^{-5}$  ampères, the current flowing through the galvanometer will be of the order of  $1.6 \times 10^{-5}$  ampères, and the resultant deflection about 160 mm., a deflection susceptible of great accuracy of measurement.

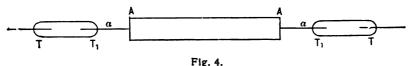
The first experiment was to place two fixed metallic brushes so as to rub on the ring under the points S and  $S_1$ . However, the friction of the brushes against the uncharged disc was sufficient to produce a deflection of about 100 mm. Moreover, the gold leaf was rapidly rubbed away, and the resistance therefore rapidly increased, so that all we could obtain from this method of procedure were rough qualitative results.

But by making yet another modification we were enabled to make quite accurate measurements. This was accomplished by employing the following exceedingly simple and effective contacts. At the extremities AA of the moving axle (Fig. 4), coinciding exactly with the axis of rotation and insulated from the axil, were fixed two very fine copper wires. Two small glass tubes,  $TT_1$ , all but sealed up at

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 $T_1$  so that the opening there was just a little larger than the diameter of the wire *aa*, were so placed that the wires turned in the openings without touching the walls of the tube. Before these tubes were placed in position they were filled with mercury and electrodes sealed in the outer ends. These contacts proved extremely satis-



factory. Their resistance when the axil was in motion remained practically the same as when the axil was at rest, an hour's running producing an increase of resistance of less than five hundredths of an ohm.

To return to the convection experiment. Two points on the ring C and D, diametrically opposite, were connected permanently to the two wires aa, which in turn were connected through the contacts to the galvanometer. If now  $SS_1$  is charged and the disc set in motion, there will be produced in the ring conduction currents distributed as explained above. But as C and D move with the disc, between these two points the difference of potential will be alternating, and consequently in the galvanometer there will be an alternating current, and hence no deflection. However, if in the galvanometer circuit is placed an interrupter actuated by an eccentric on the axle of the disc, and arranged so as to close the galvanometer circuit during the half period while CD turns from PR to RP, a unidirected current can be obtained, for the difference of potential between C and D during this interval passes from 0 to 0 through a maximum corresponding to the moment when CD is parallel to xy. The galvanometer should then show a deflection. If the eccentric is shifted 90° so as to close the galvanometer circuit a quarter of a period later, this deflection should become nil, because during the time the circuit is closed the difference of potential passes from a positive to an equal negative maximum. Between these two positions of the eccentric all intermediate deflections should be obtainable.

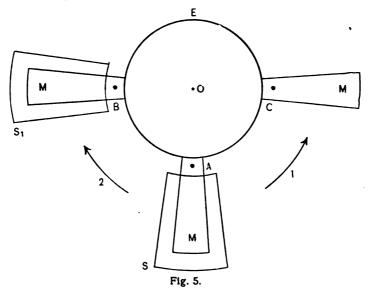
This experiment proved unusually satisfactory. The maximum deflection was quite large and the measurements made agreed within 20 per cent. with the calculated values, which, considering

the numerous approximations which must necessarily be made in determining the various constants (surface density of the charge, relative resistances of the various parts of the circuit, speed of rotation) is all that could be desired.

From these results we may therefore conclude that a charged metallic surface moving in its own plane in the presence of fixed parallel metallic surfaces carries its charge along with itself.

Experiments with Sectored Discs. Cremieu's "Open-current" Method.— Having thus solved in the affirmative the question of the existence of a magnetic effect produced by the rotation of a charged continuous disc, and verified directly the entrainement of the charge, we returned to the experiments made with sectored discs.

During the past year, Cremieu<sup>1</sup> obtained with discs formed of insulated sectors magnetic effects which were quite irregular and without any quantitative relation to the intensity of the convection



current, which, in these experiments, was measured directly. The apparatus consisted of a core of ebonite 24 cm. in diameter, carrying 18 sectors of micanite, 13 cm. long, separated from one another by 2 cm. of air. Only the outer portion of the sectors was <sup>1</sup>C. R., Vol. CXXXVI., p. 27, 1902.

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gilded, the gilt covering a width of 5 cm. The moving sectors M (Fig. 5) passed between two charged fixed sectors S, and at the same time touched a brush A connected to the earth; they therefore became charged by influence. They then passed from under the brush A and the fixed sectors S and came around under the astatic system E. Beyond the system they met a second brush B connected to the earth, thus becoming discharged. By placing a galvanometer between A or B and the earth, one could measure the charging current or the current resulting from the discharge.

Certain peculiar phenomena of solid dielectrics, first observed by Cremieu, and to which we shall return farther on, led us to employ in our joint experiments micanite sectors entirely gilded, so as to avoid all penetration of charge into the naked micanite. The astatic system was suspended in a metallic tube connected to earth. To protect this tube from the electrostatic action of the moving sectors, which were at a very high potential, Cremieu employed a paraffined tube of mica fixed directly on the metallic tube. To this disposition there are two objections. Since the bottom of the tube is small relative to the area of the moving sector, at the moment when the sector comes under the tube there is a considerable increase of the capacity of that portion of the sector directly under the tube. Consequently to this point there will be a flow of charge by conduction currents distributed in a manner impossible to calculate, which can act upon the astatic system. Secondly, in consequence of the peculiar phenomena of the dielectric to which reference has been made, the mica protector of the tube is submitted to a penetration of charge from which may result considerable perturbations. To avoid these inconveniences, in some measure at least, we left the metallic tube bare, but interposed between it and the moving sectors a large sheet of paraffined ebonite, which touched neither the tube nor the sectors.

In these conditions, the passage of the charged sectors under the astatic system produced deflections qualitatively in accord with the effects expected from the theory of convection, and properly varying with the density of the charge and the velocity. As to quantitative agreement, that was not very satisfactory, but in this form of experiment the distribution of the charge on the sectors is too indefinite to allow of even a rough approximation. Again, as the sectors rotate in the open air, it is impossible to eliminate completely the effects of the air currents, which render the system too unsteady for accurate readings to be possible.

There now remained to find the cause of the repeatedly negative results of Cremieu's experiments.

Essential Difference Between the Negative and Positive Experiments. - An analysis of the details of the negative experiments led us to see that they all differed from the positive experiments in this, that in the negative experiments the moving charged surfaces and the condensing plates, when there were any, were always covered with a thin layer of some dielectric, usually caoutchouc. In his experiments Cremieu found it desirable to realize as high a surface density of the charge as possible. To do this, he placed the turning disc and fixed condensing plates very near together, and the caoutchouc layers were for the purpose of preventing sparks between plates and discs. A priori, one could see no inconvenience resulting from the presence of the caoutchouc; in fact, one would naturally suppose that its presence would prevent leakage and ensure a more perfect entrainement of the charge, for, as the charge is carried on the surface of the dialectric in contact with the conductor, any slipping which might occur would be rendered less probable.

To test the truth of these considerations we tried the effect of covering the moving sectors in the above experiment with a layer of caoutchouc. There resulted a considerable diminution of the magnetic effect, without, however, the intensity of the convection current, as measured by the quantity of electricity going on or leaving the sectors, showing a corresponding diminution. Moreover, the nature of the deflections of the astatic system changed. At first quite distinct for the two signs of the charge, they rapidly became smaller, and at the end of several reversals became scarcely perceptible, especially when the sectors were charged positively. For the negative charge the diminution was less. Further, the deflections ceased to be proportional to the potential of the fixed sectors for voltages above 2,000 volts. Also, the charge going on the sectors became less than it should be according to calculation, and above a certain definite voltage, the charging current remained

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practically constant, no matter how much the voltage was increased.

These facts made clear the cause of Cremieu's negative results. It is to be noted, that in 1900, in his first experiments on open currents, Cremieu observed a part of these phenomena. However, as he was eager to complete his experiments on convection, he did not stop to investigate fully these effects.

We now undertook a systematic study of the rôle of the dielectric, but due to the brevity of the time at our disposal, we have not been able to carry this study very far.

As of the first importance in regard to the theory of convection, we verified the following points :

1. When the continuous discs were covered with caoutchouc, the magnetic effect diminished and presented the dissymmetry of sign observed with the sectored disc. In these experiments the charge on the discs can be determined only by measuring the potential. These measurements showed that there was the same lack of proportionality between the potential and the magnetic effect observed.

2. A thin sheet of paraffined mica fixed on the surfaces of the discs produced the same effects as the caoutchouc.

3. In Pender's induction experiment, we found that the mica diminished considerably the effects observed. For example, in one series of measurements we obtained the following deflections.

	Mm.
Discs bare, condensing plates bare,	140
Discs covered with mica, condensing plates bare,	100
Discs and condensing plates covered with mica,	15

These facts show clearly the experimental cause of Cremieu's negative results, but they do not *explain* them. Indeed, the rôle of the dielectric seems difficult to unravel from any *a priori* considerations.

From the facts observed in 1900 and in our joint experiments it seems legitimate to conclude that, when solid dielectrics are submitted to considerable penetrations of charge, they act as if they suppressed the electrostatic influence between the conductors which they separate. Moreover, for each kind of dielectric the penetration of the charge and the suppression of electrostatic influence which

results therefrom occurs at a certain well-defined voltage of the charged conductor — being independent of the value of the electrostatic field produced by this voltage. For mica the critical voltage is in the neighborhood of 4,300 volts, for sulphur between 8,000 and 12,000 volts; for ebonite, glass and paraffine the critical voltage is above 12,000 volts.

In the negative convection experiments the action of the charge on the metallic surfaces was rendered nil by the screening effect of the dielectric, or possibly by the neutralizing effect of the very considerable charges absorbed by the dielectric. But these are only suppositions — only a detailed, systematic study of these dielectric effects can clear up this very delicate point.

Study of the Amount of Charge Carried Around Under Various Conditions in the "Open-current" Experiments. — To complete our researches we undertook a study of the apparent amount of charge carried around in the open-current experiments, with the object first, to make sure if the third fundamental condition laid down at the beginning of this article was realized, and secondly, to clear up a little more the rôle of the dielectric.

The apparatus employed (Fig. 5) was the disc with the ebonite core OE carrying 18 peripheral sectors M. These passed between two fixed sectors S and at the same time touched the brush A; then, according to the direction of rotation, they either became directly discharged by the brush C, or first passed between two supplementary fixed sectors  $S_1$  and then were discharged at C. The sectors  $S_1$  formed with each sector M a capacity equal to that formed by the sectors S with M. These sectors  $S_1$ , connected to an electrometer, permitted us to see what takes place, of an electrostatic nature, in the air around the moving charged sectors. An experiment consisted in measuring galvanometrically the quantity of charge taken up by the sectors as they came under A, and the quantity of charge given up at C; also the reading of the electrometer con-

(b) On the sectors  $S_1$  the following peculiarities were observed: Suppose the disc in rotation, in the direction of the arrow 2, the sectors  $S_1$  connected to an electrometer, and all the rest of the apparatus to earth. No matter what was the velocity of rotation no deflection of the electrometer was observed. However, when the sectors S were charged, so that the moving sectors M were charged as they passed between the sectors S, the electrometer immediately took a sudden deflection, which gradually increased, the more rapidly the faster the rotation. The sign of the charge on the electrometer was the same as that of the charge on the moving sectors, while the charge on the sectors  $S_1$  was of the opposite sign, as should be expected. However, if the sectors S and M were then earthed, the deflection of the electrometer did not fall to zero, but indicated a residual charge on the sectors  $S_1$ , which charge was of the same sign as that of the moving sectors.

These facts seem to show that the rotation of the charged sectors produce in the surrounding air electricity of the same sign as that they carry. In accord with this assumption is the fact that the charging current is inferior to the discharging current. In this connection attention may also be called to the fact that the loss of charge of a body in air is considerably less when the the body is in rapid movement than when the body is at rest. This phenomenon was first observed by Matteucci.<sup>1</sup>

At present we merely state these facts with no attempt at an interpretation. It is impossible to say whether this production of charge should be attributed to the movement itself or rather to sudden variations in the field caused by the violent shocks given to the air by the rapid movement of the sectors. It should be added that we tried to detect a possible production of charge by placing in the air between a charged disc and earthed condensing plates small metallic brushes connected to an electrometer. The electrometer showed no deflection when the disc was set in rotation.

2. Moving Sectors M Bare, Fixed Sectors S Covered with Mica. — We found the same dissymmetry between the charge and discharge current as in the preceding case, and in the same direction. Further, for voltages above 3,000 volts on the fixed sectors  $S_1$  the charging

<sup>1</sup> Ann. de Chimie et de Phys., 3rd Series, Vol. XXVIII, p. 385.

current did not increase proportionally with the voltage on the fixed sectors. When this voltage reached about 4,500 volts, the charging current appeared to attain a maximum, which could not be exceeded even for a very great increase in the voltage.

Also, when the inducing sectors S were earthed after having been submitted to a charge for several seconds, the moving sectors continued to take up a charge as they passed under S, as indicated by a current continuing to flow through the galvanometer, but of the opposite sign to that impressed upon S, and this after-effect continued even for several hours thereafter without noticeable diminution. These phenomena were extremely irregular, the size of the supplementary currents seeming to depend upon the previous state of the mica and the duration of the experiments.

At the sectors  $S_1$  the same phenomena were observed as in the preceding case.

3. Moving Sectors M and Fixed Sectors S Covered with Mica. — As long as the potential of the fixed sectors S was below 2,000 volts no anomalies were observed. Above 2,000 volts the charge current became considerably greater than the discharge current. The dissymmetry attained even as much as 30 per cent. In the neighborhood of 4,500 volts, the proportionality between voltage and charge current ceased, as in the preceding case. There were also supplementary currents after the inducing sectors were earthed. These could attain as much as 50 per cent. of the value of the normal currents when the inducing sectors were charged. But there was this peculiarity, that for the moving sectors charged positively they were in the opposite direction to the normal currents, while for the moving sectors charged negatively they were in the same direction as the normal currents. The sectors S, took up no charge by influence. Even more so than in the former case did all these irregularities depend on the previous state of the dielectric and the duration of the experiments.

All this shows how complex the phenomena are, and that only a prolonged study can fully explain them. This much seems certain, that there is a penetration of charge in another sense from that usually understood by the expression. That which seems to prove this most conclusively is that, in the third case above, the supple-



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mentary currents are obtained only when the two brushes A and C both make contact with the sectors. If either of the brushes is suppressed, there is no longer a supplementary current. If the supplementary currents were due merely to the ordinarily considered absorbed charge, this charge would gradually flow out through the brush left in contact, and therefore produce a current in the galvanometer, without the presence of the second brush being necessary. It seems to us that the mechanism of the supplementary currents is analogous to that of an electrophorous, the mica on our sectors in some way or other, being electrolyzed.

It is essential, in any case from the point of view of the accepted theories, to know why the dielectric diminishes or suppresses the magnetic effect, and what is the nature of the action of penetration.

*Conclusions.* — All that can be said at present of these accessory phenomena is that they do not permit us to affirm with certainty that the third fundamental condition of a correct convection experiment is exactly fulfilled, particularly with sectored discs. But the following conclusions are certainly legitimate.

1. A charged continuous metallic surface turning in its own plane opposite fixed parallel condensing plates carries its charge with itself.

2. The *entrainement* of this charge produces a magnetic field in the direction demanded by the assumption of a magnetic effect due to electric convection, and in accord with the calculated value to 10 per cent.

3. Charged isolated sectors, moving in their own plane, without the presence of any condensing plates, produce a magnetic effect in the direction and of the proper size demanded by this same assumption.

It is not for us to say if these magnetic effects are really due to electric convection in the sense in which Faraday and Maxwell understood this expression, nor to decide if they are in accord with the fundamental hypotheses of the present theories.

## MEASUREMENT OF AIR VELOCITY AND PRESSURE.

#### Ву А. Г. ΖАНМ.

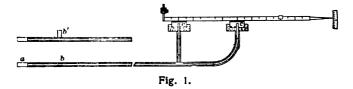
FOR general service in aërodynamic experimentation two kinds of anemoneter may be useful, one measuring air velocity, the other air pressure. Sometimes the velocity alone is required; again the pressure, either static or impactual, is mainly to be determined. In either case an accurate and faithful instrument is most desirable. Of course the impact can be calculated from the velocity, and *vice versa*, providing all the data are at hand for computing the density of the moving fluid. But when many exact determinations have to made, it is well to evade such calculations by choosing the appropriate anemometer; that is to say a velocity instrument for measuring velocity, and a pressure instrument for measuring pressure, or impact. One thereby saves much labor, and avoids the errors that may result from misreading the elements of density.

Suppose, for example, that one is finding the head resistance of various models in terms of the wind speed, observing the latter by means of a velocity anemometer. The wind speed may be kept constant throughout the research, but the resistance of any given model will vary day by day, and hour by hour. Every three degrees change of the thermometer, or eight millimeters change of the barometer, will alter the resistance one per cent. Even the variations of moisture may make a perceptible difference. So, in order to compare the resistances obtained at different periods, it is necessary to reduce them all to standard atmospheric conditions. This means a great deal of labor and many unwelcome errors. On the other hand, if a pressure anemometer is employed, all these troubles will be avoided. So long as its readings are kept constant the resistance of the models must remain constant, no matter how the atmospheric conditions may change. Thus all the observations of an extended research may be compared without reduction. In fact, for

impact measurements the pressure anemometer has three distinct advantages: (1) Computations are avoided, (2) readings of temperature, pressure and saturation are unnecessary, and errors from that source obviated, (3) the anemometer readings and model resistances may be plotted while the experiment is in progress, thus revealing observational errors which may at once be eliminated by taking new readings where required. In a similar way it-may be seen that the velocity anemometer has equal advantages in many important investigations.

So the need of two kinds of anemometer is a very real one; and it would be well if they were standardized to measure accurately to say one per cent. throughout a wide range of velocities. At present no such instruments are offered in the market, though possibly some of the types in use could be standardized to that degree of accuracy, particularly the screw, the cup, and the pressure-tube varieties. But thus far the calibration of such instruments has proved difficult and not completely satisfactory. Indeed it would be an advantage if the anemometers were free from empirical constants, so as not to require calibration at all.

The present paper treats of the design and use of an anemometer<sup>1</sup> whose observed indications seem to conform to those computed for it from theory. The data submitted were obtained hurriedly, as



incidental to other measurements, but it is hoped they are accurate enough to establish confidence in this type of instrument; for it is easy to construct, convenient to use, adapted to a wide range of velocities, and has no empirical constant.

The anemometer is an adaptation of the Pitot tube, and consists essentially of a double pressure nozzle in connection with a delicate pressure gauge. The assembled parts are shown in Fig. 1.

<sup>1</sup>This instrument was exhibited before the Washington Philosophical Society, May 24, 1902.

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A "pressure-tube" held along stream transmits the impact pressure of the air from nozzle a, the static pressure from nozzle b, to the cups c, of a differential pressure-gauge. These cups, symmetrical in size and placement, are inverted over coal oil, and counterpoised from a meterstick. A sliding weight, and a pointer measure the difference Letween the static and kinetic pressures at the double nozzle; and from this can be computed the speed of the air, if its factors of density are simultaneously observed; that is its temperature, pressure and saturation.

We may notice some elements of construction, then the theory and test of the instrument, and finally a few of its applications.

In designing the pressure-tube it is well to select the largest pipe that can be conveniently employed, so that the air within may quickly come to rest after any displacement. The one here shown has an inch and a quarter outer pipe, a three quarter inch inner pipe, each ten feet long and connected by three quarter inch rubber hose to cups measuring one hundred square centimeters in cross-section. The counterpoised beam responds quickly to the varying impulses of the wind, whereas with quarter-inch hose of ten feet length, the motion is tediously slow, owing to the great viscous resistance of the air in such narrow channels.

Almost any size and form of nozzle will convey the impact perfectly, providing it squarely face the wind. All sizes of pipe, from a lemonade straw to a milk-can show exactly the same pressure. All shapes, cylindrical, conical, hemispherical; all thicknesses of wall give identical results.

But the static nozzle must be designed with some care. It should occupy a part of the tube where the stream-lines are undisturbed, and be so shaped as not to deflect the air blowing over it when the cups are at rest. The nozzle here outlined has two longitudinal slots cut into opposite sides of the outer pipe, one foot from the end, each slot being one eighth inch wide by three inches long. As will be shown presently, this nozzle seems to give the true static pressure of the passing wind-current.

The cups may be rigidly attached to the beam, or hung like the pans of an ordinary balance. To avoid excessive stability, owing to the buoyancy of the cup walls, it is well to make them of the AIR VELOCITY.

thinnest metal practicable. For very delicate work it is essential that the liquid flow freely along the cup walls, so as to minimize the effect of surface tension; also the pointer excursion must be limited to a narrow range by suitable stops. If its swing is large the liquid trickling down the cup walls will materially alter the readings, unless a long time is allowed the pointer to come to rest.

The cups here shown have brass walls one hundredth of an inch thick, whose effective buoyancy is nearly one per cent. of the pressure on the internal cup base. The coal oil flows freely along their sides, practically eliminating the objection of surface tension. The pointer swings ten millimeters to either side of the zero, the cup displacement being two millimeters. With these limited excursions the trickling of the oil is practically unobjectionable, except for the most delicate measurements. For these, of course, the pointer can be still further limited. The buoyancy also, is unobjectionable. It is too small to impair the sensibility, and, since its effective lift per unit of surface is precisely equal to that of the air inside the cup, the total lift equals the product of the air pressure by the area of the external base of the cup.

The graduations are found to be convenient in use. The beam is a meter stick carrying a sliding weight and pointer, each of which gives the air pressure in milligrammes per square centimeter, that is to say in millionths of an atmosphere, approximately. The scale can be made to show less than one tenth of this when the pressure is sufficiently steady, which, however, does not occur in anemometry.

So much for the details of construction and practical operation.

The hydrodynamic principle of the double pressure nozzle is contained in Bernouilli's theorem. For present purposes, however, we may suppose the density of the air constant, its flow uniform and level. Bernouilli's theorem may then be stated as follows: At all parts of a stream-line the velocity head plus the pressure head equals a constant. Or otherwise :

$$\frac{\rho v^2}{2g} + p = p_0, \tag{1}$$

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total head, or pressure at a point where the velocity is zero. Hence, if the nozzle will measure the differential pressure  $p_0 - p$ , we can at once compute v therefrom.

A. F. ZAHM.

To prove formula (1) let us take the general stream-line equation (Lamb's Hydrodynamics, \$24) for adiabatic expansion :

$$\frac{v_1^2 - v_2^2}{2g} = \frac{\gamma}{\gamma - 1} \frac{p_2}{\rho_2} \left[ 1 - \left(\frac{p_1}{p_2}\right)^{\gamma - 1} \right],$$

 $v, p, \rho$  being the velocity, pressure, density, at any one point of the stream-line;  $v_2, \rho_2, \rho_2$ , like values at any other point. Let  $v_2 = 0$  be the velocity at the impact mouth of the pressure-tube,  $v_1$ , the velocity in the unchecked stream, and write  $p_1 = p_2(1 - x)$ . Then the general equation can be written:

$$\frac{\rho_1 v_1^2}{2g} = \frac{\gamma}{\gamma - 1} \frac{\rho_1}{\rho_2} p_2 \left[ 1 - (1 - x)^{\frac{\gamma - 1}{\gamma}} \right]$$
$$= \frac{\rho_1}{\rho_3} p_2 \left( x - \frac{x^2}{2\gamma} + \frac{1 + \gamma}{6\gamma^2} x^3 - \cdots \right).$$

Now  $x = (p_2 - p_1)/p_2$ , is usually very small; its largest value in this research being about 0.001; also  $\rho_1/\rho_2$  differs from unity by less than 0.001, and  $\gamma = 1.408$ . Hence the equation reduces to:

$$\frac{p_1 v_1^2}{2g} = p_2 x = p_2 - p_1,$$

which is true to less than 0.1 per cent. for the range of velocities employed. Or, changing the notation, we have the formula :

$$\frac{\rho v^2}{2g} + p = p_0,$$

in which p is the pressure in the unchecked stream,  $p_0$  the pressure in the impact mouth of the tube.

To demonstrate experimentally that the pressure  $p_0$  is equal to the total head pressure, the following plan was pursued. A tube



inch in diameter, held in the center of this tube, transmitted the impact of the inrushing air to one cup of the pressure gauge, the other being connected with the quiet part of the tunnel. The gauge reading was taken; then the nozzle was thrust through the inlet tube toward the outside of the tunnel, and finally clear outside. No appreciable change of pressure could be noticed, thus showing that an impact nozzle sustains a constant pressure at all points of a stream-line, and that this is equal to the total head pressure. Again, the impact pressure was read at five different fan speeds, the nozzle being held first in the quiet outer atmosphere, then at the center of the inlet tube. The readings agreed to less than one per cent., as exhibited by the subjoined table.

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IA	BLE	1.

Comparison (	of Total Head and	Impact Pressure at	Point of Greatest Velocity	1.

JFan Speed.	Total Head.	Impact Pressure at Center of Inlet.
rev. min.	mg. per sq. cm.	mg. per sq. cm.
150	540	538
170	680	678
200	850	847.5
225	1,000	997.5
245	1,100	1,108

If it could be shown with equal exactness that the side nozzle measures the static pressure of the fluid gliding over it, the theory of the pressure tube would be completely verified. It is easy to measure the actual pressure sustained by the side nozzle at any point of the stream, but not so easy to prove the observed pressure equal to the true static pressure at the point, except where the velocity is zero or a maximum. It is zero where the stream tube is very broad, say in the reservoir, and here, of course,  $p = p_0$ ; it is a maximum where the air rushes freely through the inlet tube, and here the static pressure must, according to theory, be equal to the pressure inside the tunnel. In fact when a narrow static tube, held at the center of a large inlet, was connected with one cup of the gauge, while the other cup was joined by hose to the quiet part of the tunnel, no material difference of pressure was observed. Hence we may conclude that the observed pressure equals the true static

pressure for that particular velocity. The experiment was made at five different fan speeds with like result.

It thus appears that for all the velocities employed, which extended from five to thirty miles an hour, the impact nozzle sustains exactly the pressure  $p_0$ , the static nozzle the pressure p. Hence, when the two nozzles a, b, Fig. 1, are connected simultaneously with the pressure-gauge, as is regularly done in practice, their differential pressure  $p_0 - p$ , must be an exact measure of the quantity  $\rho v^2/2g$ , and therefore determines the true velocity of the air. Now, by equation (1),  $\rho v^2 = 2g(p_0 - p)$ ; or, writing  $k = \sqrt{2g/\rho}, \delta = p_0 - p$ , the velocity is:

$$v = k \mathbf{1} \ \delta. \tag{2}$$

In practice the differential pressure,  $\partial_i$  is read directly from the instrument in milligrammes per square centimeter, and k is computed from the observed elements of density. Thus for dry air at 0° Centigrade and a megadyne per square centimeter pressure,  $\rho = 1.2759$  grammes per liter, whence  $k = \sqrt{2 \times 980.96} \div 1.2759$ = 39.21 for the latitude of Washington, and the velocity in centimeters per second is :

$$\tau = 39.21 \, V \, \delta.$$

For air at any temperature, pressure and humidity (Minchin's Hydromechanics), the density is :

$$\rho = 0.4645 (8p - 3f) \div 8T;$$

p being the barometric pressure in millimeters, f the aqueous vapor pressure, T the absolute temperature Centigrade. From this k can be computed for any observed atmospheric conditions.

As a further test of the accuracy of the pressure-tube anemometer, its readings were compared with those of another instrument, designed with a special view to precision rather than convenience. Ten observations of the wind speed were taken simultaneously with both anemometers, and their average values agreed to less than one per cent. This extra instrument, which is sometimes used to standardize others, may be called the balloon anemometer. A brief description of its plan and performance may be worth a passing notice.

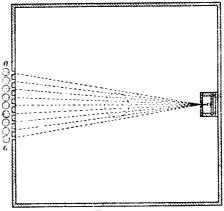
#### AIR VELOCITY.

A toy balloon is held at the center of the wind-tunnel, between the prongs of a fork, one prong being firmly moored to the wall by a thread, the other joined to a release string. When the string is jerked the fork spreads and the balloon floats along the wind-current without rotation. After drifting less than eight feet it has acquired the full velocity of the wind, as may be proved by projecting

the balloon with like speed in still air and observing how far it moves before coming practically to rest.

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To find the velocity of the balloon two thin pencils of light are thrown squarely across its path and the time of transit recorded by a camera designed for that purpose. The general plan of the apparatus is shown in Fig. 2.





A bank of incandescent lamps a, a, shining through one-eighthinch holes in the tunnel wall are brought to focus on a very sensitive photographic plate b. Ten feet farther along the tunnel a like thing occurs. The plates are clamped to a ten-foot board which is drawn by hand along grooves inside the camera box, the box itself being thirteen feet long. The images of the incandescent carbons trace, along each plate, fine straight lines which are momentarily interrupted by the passing balloon. The method is an adaptation of that used by the writer to measure the velocity of projectiles.<sup>1</sup>

To time the plate an electric tuning-fork interrupts one of the light beams 128 times a second, making the record a dotted line. After development the plate records are superposed and the number of vibrations counted from center to center of corresponding balloon breaks. This gives the time of transit of the balloon over the tenfoot stage from center to center of the light a second and thereby

accurately to less than one part in five hundred. For greater exactness the circuit is broken, and the fork vibrates freely during the balloon flight.

The accompanying table gives the data for ten observations at practically the same wind velocity. Measurements were not made at other speeds for lack of time.

T/	ABLE	II.

Comparison of Balloon Flight and Pressure-tube Readings. Barometer, 746.51 mm.; Temperature, 284° C.; Saturation, .50.

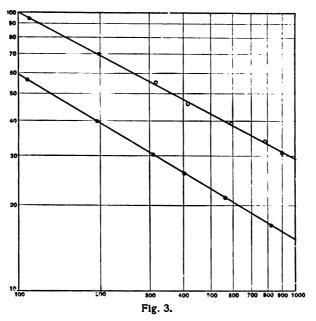
	Tuning-Fork	Velocity of Wind in Tunnel.		
Readings.	Vibrations.	By P. Tube.	By Balloon	
mg. per sq. cm.		ft. sec.	ft. sec.	
36.5	163.5	7.96	7.85	
36	162.3	7.90	7.90	
36	163.5	7.90	7.85	
36.5	166.0	7.96	7.73	
39.5	157.4	8.27	8.16	
37.25	156.2	8.03	8.20	
36	156.8	7.90	8.18	
36.5	157.8	.7.96	8.12	
36.5	171.3	7.96	7.50	
38.5	161.0	8.16	7.96	
		mean 8.00	mean 7.95	

The results show that the average air velocities, as determined by two such widely different instruments, agree to less than one per cent. The coincidence is rather too close to be representative; still the general agreement is such as to establish confidence in this form of pressure-tube anemometer, at least for the velocity at which the test was made. To assure ourselves that the instrument is reliable at other velocities, we may recall the experimental proof that each nozzle sustains exactly the theoretical pressure at all speeds up to thirty miles an hour.

Incidentally, in the course of other measurements, this anemometer has been compared with several instruments of a different type; notably two cup anemometers, a large and a small one, used by the United States Weather Bureau; a screw, and a cup anemometer employed at the Smithsonian Institution; and a Dines pressure-tube anemometer.

AIR VELOCITY.

The following page from the laboratory note-book illustrates the calibration of the first instrument mentioned. It was placed in the tunnel beside the pressure-tube in such a way that neither interfered with the other. The time of fifty revolutions of the cups was indi-



cated by an electric bell, and the interval between two or more ringings of the bell was measured by means of a stop watch reading to quarter seconds. The readings of the pressure gauge were simultaneously noted.

TABLE III.

Comparison of Standard Pressure-Tube Anemometer and Four Inch Cup Anemometer of the U. S. Weather Bureau. Barometer 30'.473, thermometer 3°.5 C.

Date.	Fan.	Pressure Tube.	Wind Speed.	4" Cup Ane- mometer.	Wind Speed.
Feb. 20, '03	rev. min.	mg. sq. cm.	mi. hr.	sec. in 50 rev.	mi. hr.
2.15 p. m.	150	43	5.7	62.5	5.8
- 1	200	83	7.9	44.5	7.9
	250	120	9.5	35.5	9.7
· .	300	180	11.7	29.0	11.7
1	350	250	13.7	23.5	14.0
3.15 p. m.	400	295	15.0	22.0	14.9
- 1	450	350	16.2	19.6	16.5

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By comparing the wind velocities indicated by these two instruments it will be seen that they differ by less than two per cent. This is the case under favorable circumstances, when due attention is given to the working condition of the instruments; but, if they are not very carefully used, the discrepancy may exceed five to ten per cent. of the quantity measured.

In a similar way the calibration of the small Weather Bureau instrument, known as a kite anemometer, having cups one inch in diameter, and four inches from center to center, gave the following values.

TABLE IV.

Comparison of Standard Pressure-Tube Anemometer and One Inch Cup Anemometer of the United States Weather Bureau.

Date.	Fan.	Pressure- Tube.	Wind Speed.	Cup Anemometer.	Wind Speed.
Jan. 3, 1903.	rev. min.	mg. sq. cm.	mi. hr.	sec. in 500 rev.	mi. hr.
2.15 p. m.	200	110	9.53	121.25	9.45
	300	220	13.46	83	13.8
	400	370	17.46	65	17.55
	500	570	21.68	51	22.35
2.55 p. m.	600	830	26.14	41.5	27.4

The results obtained in standardizing the anemometers of the Smithsonian Institution are given diagrammatically to show the concordance of the observations. They were obtained in less than an hour for each instrument, without special pains; yet the data seem to harmonize very well, and to indicate that such instruments may give quite accurate readings when used with due care. One is a cup anemometer having cups one inch in diameter, and three and three eighths of an inch from center to center; the other is a Beck screw anemometer, two and five eighths of an inch in diameter, and having flat blades. The data are plotted on logarithmic crosssection paper for convenience, their relation being expressed by a

notably in the meteorological service. The essential difference in principle between the Dines pressure-tube and mine consists in the

form of the static nozzle, which in his instrument is a punctured dome whose axis is at right angles to the steam-lines (see Fig. 4), while in mine it is a hole, or slot, so placed as not to deflect the steam-lines.

In order to compare the two instruments, the Dines static nozzle was employed as shown in Fig.  $\rightarrow$  E I, b', and readings taken at several different fan speeds. Then similar readings were taken with the pressure tube shown in Fig. I, b, under the same weather conditions. The results are presented in the accompanying table, and plotted to the same scale on logarithmic cross-section paper, as shown in Fig. 5.

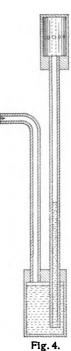
The readings obtained with the Dines nozzle are approximately 1.46 times those found with the steam-line nozzle, for the velocities employed, which ranged from ten to twenty-five miles an hour. This excess is doubtless due to the suction in the rear of the punctured dome which con-

stitutes his static nozzle. The dome, therefore, possesses the advantage of magnifying the readings of the instrument. Its hydrodynamic theory, however, is different from that of the streamline nozzle, and its readings cannot be calculated from equation (2) of this paper.

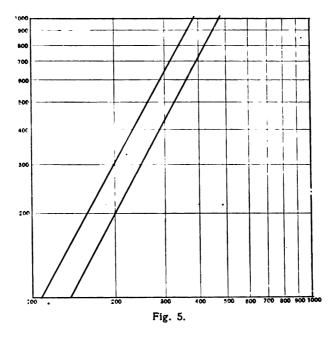
TABLE V.

Fan Speed.	Pressure-Gauge R	Pressure-Gauge Readings, $p_0 - p$ .		
ran opeea.	With Stream-Line Nozzle.	With Dines' Nozzle.	Ratio.	
rev. min.	mg. sq. cm.	mg. sq. cm.		
200	205	305	1.50	
250	310	460	1.48	
300	440	640	1.46	
350	590	850	1.44	
400	760	1,080	1.42	

Comparison of Stream-Line Static Nozzle with Dines' Nozzle.



It would be interesting to find a theoretical formula that would give, for Dines' instrument, the exact relation between the wind velocity and the differential pressure. For the range of velocities shown in Table V., the formule  $v = k' \sqrt{\delta}$ , will apparently give the true wind speed, if 1.46k' equals k of formula (2). But the comparison was too briefly made to be conclusive. Besides the formula thus obtained is only an approximate one, and does not free the instrument from an empirical constant.



Various other forms of static nozzle have been used by different experimenters. The simplest of these is a straight open-ended tube, standing at right angles to the current. Another form consists of two thin circular discs, placed very near together, their axis perpendicular to the current; and in the modification used by Professor Nipher, a sheet of wire gauze fills the space between the discs, protruding slightly beyond their edges. Neither of these nozzles, however, has been compared with the one discussed in this paper.

I would refer the reader interested in the pressure-tube, as an instrument for measuring the velocity of liquids, to a very careful and valuable paper by Mr. W. M. White, read before the Louisiana Engineering Society, May 13, 1901, and published in the Journal of Engineering Societies the following August. His methods of experimentation were quite different from the ones here outlined, but they established conclusively the theory of the pressure nozzle for water. Indeed this is as it should be, since the equation of motion is the same in both cases. Thus the two researches corroborate one another, if the excellent work of Mr. White can be said to need any confirmation.

In conclusion it is a pleasure to acknowledge my indebtedness to Mr. D. W. Taylor, Naval Constructor U. S. N., for his kind interest in this work. Indeed it was at his suggestion that the present investigation was taken up. He was making, for the government, a study of the ventilation of ships, with a view to determining the efficiency of different fans, and the most favorable working conditions of the ventilating system. He relied upon the Pitot tube to determine the flow of air at various points of the ventilating pipes, and, in October, 1902, expressed the wish to have its accuracy tested in a wind current of known velocity. This led to the device which I have described as the "balloon anemometer." The apparatus was made, and the observations were taken in November, 1902.

I have also to thank Professor C. F. Marvin, of the Weather Bureau, and Mr. C. M. Manly, of the Smithsonian Institution, for many valuable suggestions, for the use of a variety of anemometers, and for important literature and references pertaining to this work.

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[VOL. XVII.

# SECONDARY RADIOACTIVITY IN THE ELECTROLY-SIS OF THORIUM SOLUTIONS.

#### BY GEORGE B. PEGRAM.

I T being a well-known fact, studied especially by Rutherford and Soddy,<sup>1</sup> that the surface of bodies in the air near thorium compounds becomes charged with a temporary radioactivity under the influence of the thorium emanation, and that this activity is much increased if the surface is negatively electrified, it seemed probable that some interesting results might be obtained in connection with the electrolysis of solutions containing salts of thorium. Accordingly solutions of thorium nitrate were subjected to electrolysis, the electrodes being of platinum, with the general result that the anode became more or less radioactive. This radioactivity was only temporary, in some cases decaying at the rate of half its intensity in eleven hours, in other cases much more rapidly. The secondary activity due to the emanation from dry thorium oxide decays at the rate of half its value in about eleven hours, according to Rutherford.

The thorium salt used in most of the experiments was a so-called chemically pure thorium nitrate, prepared from Brazilian monazite by E. de Haen, of Hanover, and sold by the firm of Eimer and Amend, of this city. When not otherwise specified this is the thorium nitrate referred to throughout the paper. From solutions of this salt an adherent anode deposit varying in amount from a slight tarnishing of the platinum to a reddish brown or sometimes brassy colored coating was obtained. This coating was found to be highly radioactive. Some comparisons between its activity and

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found it to be lead peroxide. The presence of this matter which is deposited on the anode proves the impurity of the thorium nitrate, but the phenomena are none the less interesting.

If a solution of very pure thorium nitrate is used for electrolysis very little matter is deposited on the anode and the resulting activity of the anode is comparatively small. Three samples of especially purified thorium nitrate were very kindly furnished me by some chemist friends, Mr. Neish of our department of chemistry, Professor Baskerville of the University of North Carolina, and Mr. Whitaker, chemist of the Welsbach Gas Mantle Company. From none of these could any visible deposit be obtained on the anode, yet after electrolysis for considerable periods the anodes showed a certain amount of activity, though small in comparison to that of the deposit from the de Haen thorium nitrate and differing from it in its rate of decay.

If to a solution of pure thorium nitrate is added a small amount of some salt such as lead nitrate or copper nitrate, a metallic kathode or oxide anode deposit may be obtained, and such deposits are found to be radioactive.

One might expect that the kathode in electrolysis would collect a larger amount of radioactivity than the anode, since in the air near thorium compounds a negatively charged body, or kathode, becomes more active than an uncharged or positively charged body. Such is not the case in the electrolysis of thorium solutions. Α small amount of thorium hydrate is generally deposited on the kathode during the electrolysis, but the temporary activity so noticeable on the anode is not present on the kathode. Since the thorium hydrate deposit can only be removed from the kathode by such treatment as would also remove the secondary activity if present, the kathodes tested for radioactivity were simply washed after the electrolysis and their activity tested at intervals over a period of several days, during which time no change could be detected in their activity, from which it is inferred that the total activity was due to the constant activity of the thorium hydrate. If a very heavy current density is used in the electrolysis the thorium hydrate comes down at the kathode as a somewhat gelatinous precipitate, which is redissolved on standing by the nitric acid from the anode.

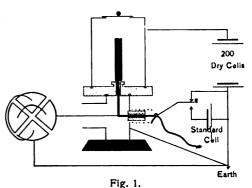
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The present paper is then an account of a number of experiments in connection with the radioactivity of the peroxide of lead deposit from the de Haen thorium nitrate solutions, of the anodes used in pure thorium nitrate solutions, of the anode and kathode deposits from salts introduced into the thorium solutions, of the gases liberated by electrolysis, and some other related matters. A previous short paper on the subject was read by title at the Pittsburg meeting of the American Physical Society, June, 1902, and an abstract printed in Science, November 21, 1902, p. 825. Other experimenters who have subjected radioactive solutions to electrolysis have been Dorn,<sup>1</sup> who found that on the electrolysis of solutions both the anode and kathode become temporarily radioactive, the anode more strongly so; Sella, who electrolyzed thorium solutions and found both anode and kathode temporarily radioactive; and Marckwald, who has obtained a new radioactive substance resembling tellurium by the electrolysis of solutions of polonium.

Apparatus. — Electrolysis of the thorium solutions was generally performed in a straight-walled glass beaker, 6 cm. in diameter. For anodes hollow cylinders of platinum, 8 cm. long, 1 cm. diameter, were used, the open lower end resting on the bottom of the beaker, so that the inside of the cylinder should take no part in the action. A sheet platinum kathode, just fitting inside the beaker, was used, the anode being placed in the middle of the beaker. With 100 c.c. of solution 3.5 cm. of the anode was immersed, giving an anode surface of 11 cm<sup>2</sup>. Current was obtained from the 115volt lighting circuit, resistance being introduced into the circuit to regulate the amount of current. The current was measured by a voltmeter, graduated in thirtieths of a volt, across a 5-ohm resistance in series with the electrolytic cell. Low voltage current was obtained by shunting the electrolytic cell with a variable resistance. The voltage of the circuit was fairly constant, so that the variations of current were within the errors of measurement of the radioac-

The radioactivity of the anode was measured by the conductivity it imparted to the air in a testing vessel, consisting of a metal cylinder 13 cm. high, 10 cm. in diameter, with removable lid, standing on a hard-rubber base. A brass rod, over which the cylindrical anode could be slipped, stood up through the middle of the base,

below which it was connected to one pair of quadrants of an electrometer, the end of the rod below the hard-rubber base, and the short wire leading to the electrometer being surrounded by a grounded metal tube. This rod, and therefore the electrometer



quadrants, was ordinarily grounded through a spring contact piece, but a slight pull on a string served to break the contact. The metal cylinder was connected to the negative pole of a battery of 200 dry cells (280 volts). When a radioactive anode is slipped over the central rod, the air in the vessel is ionized by the radiations and conduction takes place across the air column, thereby causing the electrometer needle to move at a rate proportional to the current. The voltage used was sufficient to utilize practically the total conductivity of the air column, and thus to obtain the maximum current. It has been shown <sup>1</sup> that under these conditions the current between the cylinder and central rod is very nearly proportional to radioactivity of the surface of the central rod.

The electrometer used is of the Dolezalek<sup>2</sup> quartz fiber suspension type, constructed in the department shop. Amber insulation, which is excellent even in comparatively damp air, supports the quadrants. The needle is of hard rolled aluminum foil .001 inch thick, of the Maxwell pattern and 3.8 cm. long. The use of a single piece of aluminum has some obvious advantages over the double thickness gilt paper needle of Dolezalek, especially as to

> <sup>1</sup> E. Rutherford, Phil. Mag., February, 1900. <sup>2</sup> Zeit. fur Inst., December, p. 345, 1901.

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lightness and permanence of form under varying hygrometric conditions, though the damping is not quite as great as with the paper The needle was charged by being kept in connection needle. through the suspending quartz fiber, which had been dipped in a solution of calcium chloride, with the negative pole of a battery of 100 dry cells (140 volts), and at this voltage usually gave a deflection of 360 mm. divisions on a scale 130 cm. away when a Clark cell was connected in between the quadrants. The Clark cell could be thrown in by simply pressing a key and was used not only for checking up the sensitiveness of the electrometer, but also for quickly bringing the needle to rest at zero after a reading, since the suspended system was not quite dead-beat. The electrometer has been used for weeks without changing its sensitiveness more than 2 or 3 out of 360 divisions. Sometimes the electrometer had to be moved and then its sensitiveness changed, so that all the measurements which are compared with one another are reduced to the same electrometer sensitiveness by applying the ratio of sensitiveness on the two occasions as determined by the Clark cell, which gives a result very nearly correct, though it is true that the changes of sensitiveness to difference of potential and of sensitiveness to quantity of charge do not necessarily take place in the same ratio. In some of the measurements it was necessary to decrease the sensitiveness of the electrometer very much, and to do this a small leyden jar, capacity .0005 microfarad, was connected to the electrometer and testing vessel. This decreased the rate of movement of the needle with a given current to .115 of its rate without the jar attached, so the capacity of the testing vessel and electrometer is  $.627 \times 10^{-4}$ microfarad. With the usual sensitiveness of 360 divisions to 1.43 volts a rate of I division per second corresponds to a current of  $2.5 \times 10^{-13}$  ampere through the testing vessel. There was always a small leakage from the testing cylinder to the electrometer, usually amounting to .13 division per second. It was quite constant and

the absorption of the radiations by different thicknesses of aluminum. At the same time a radioactive gas similar to the thorium emanation is given off, which remains in the air of the testing vessel, giving it considerable conductivity for a few minutes after the active anode is taken out of the testing vessel. The conductivity is proved to be due to a radioactive substance in the air inside the testing vessel by the fact that when the air is blown out of the testing vessel the conductivity immediately drops to zero.

The following measurements made on an anode made quite radioactive show the penetrating power of the radiations through aluminum. The aluminum was in the form of cylinders of foil fitting closely around the radioactive anode. When no foil was used the conductivity of the air column, with this particular anode, was too great to measure without changing the electrometer arrangements, so a cylinder of lead with a longitudinal slit to expose one fifteenth of the active surface, was put over the anode and the resulting electrometer rate multiplied by 15.

Anode with Radioactive Coating from the de Haen Thorium Nitrate.			
No. Thicknesses of Al. Foil, .04 mm. Thick.	Electrometer Divisions per Sec.		
0	4,000		
1	417		
2	41		
4	24		
7	19		
11	18		
15	12		

The question whether or not the ratio of radioactivity to mass of the lead peroxide deposit was constant during all stages of the electrolysis was investigated by using successive anodes in the solution for definite periods of time, and testing their activity, after which the deposit was dissolved off and the loss of weight determined. The balance used was sensitive to  $\frac{1}{10}$  mg., but this of course did not enable a very accurate measurement of the mass of the deposit to be made, since the total mass was so small.

The small Leyden jar was connected to the electrometer during the measurements. Without it the number of divisions per second above would have been nearly nine times as great, too fast a rate to measure. It appears from the variation in the ratio of the activity to

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An	ode 1	Used.	Mass of Deposit.	Elec. Div. per Sec.	Ratio Activity to Mass
First	20 n	ninutes.	2.8 mg.	60	1.00
Next	20	"	2.1	43	.94
	60	"	2.0	100	2.3
**	20	"	.3	13	2.0

Solution, 15 gm. thorium nitrate in 100 c.c. water. Current .84 ampere.

the mass that the more slowly the matter is deposited the greater its activity.

The Effect of Continued Electrolysis. — The following results show how the activity of the anode when used in a solution of the de Haen thorium nitrate rapidly decreases with the duration of the electrolysis, due chiefly to the decreasing amount of the brown deposit on the anode. The experiment consisted in putting in fresh anodes at intervals as the electrolysis proceeded for periods of five minutes and testing the resulting radioactivity of the anodes.

Solution of 40 gm. Th(NO<sub>3</sub>)<sub>4</sub> in 400 c.c. water. Current .44 ampere.

Duration of	Electrolysis.	Activity of Anode, Electrometer Divs. per Sec.
5 u	ninutes.	12.50
15	**	(50.00)
5	<b>66</b>	11.55
35	"	
5	<b>6</b> 6	6.25
35	46	
5	"	2.70
75	"	
5	4.6	1.62
365	**	
5	<b>6</b> 6	1.25

Thus by 475 minutes' electrolysis with the current strength as above the power of the solution to deposit radioactive matter on the anode had decreased to one tenth of its original amount. No doubt if the solution could be kept perfectly neutral the lead peroxide would come down faster, for the presence of free nitric acid around the anode tends to keep it in solution. After long electrolysis, when there is no longer any visible amount of matter deposited on the anode, the

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comparable to that obtained from the purest thorium solutions, so that it represents perhaps a deposition of radioactive matter unmixed with any ordinary matter from the solution.

It seemed probable that the radiations from the thorium salt itself might be changed in quality or quantity after being in a solution subject to electrolysis. The oxide being more convenient to work with than the nitrate, 100 mg. thorium oxide was prepared from the nitrate by heating it to a low red heat, and also 100 mg. from nitrate from a solution that had undergone long electrolysis, until very little radioactive matter was being deposited on the anode. The activity of the two samples of oxide was practically the same in amount, but the oxide from the nitrate that had been in the solution seemed to give off a slightly smaller amount of the radioactive emanation.

Activity of Anode as Related to the Amount of Thorium Salt.— The activity of the anode depends, other conditions being the same, on the total mass of the thorium nitrate used in the solution, except when dilute solutions, less than 2 gm. to 100 c.c., are used. Solutions of 100 c.c. water with different amounts of thorium nitrate were made up and subjected to electrolysis with equal currents for equal times and the activity of the anodes tested.

Time of electrolysis in each case five minutes. Current .44 ampere.

	Solu	tion.	Activity of Anode, Electrometer Diva. per Sec.
1.25 gm	1. Th(NC	) in 100 c.c. water.	1.85
2.50	""	**	3.03
5.00	**	""	6.45
10.00	"	66	15.8
20.00	**	**	31.3

With the exception of the first and weakest solution the activity increases pretty regularly with the amount of thorium salt in solution. Other experiments with dilute solutions showed considerable irregularity in the results.

If we keep the total mass of thorium nitrate constant, but vary the concentration of the solution by increasing the volume of water, not much difference is found in the activity of the anode. From 2.5 gm. thorium nitrate in 100 c.c. water, the anode gave 3.03

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electrometer divisions per second, from 2.5 gm. in 200 c.c. water, the rate was 3.80 divisions per second.

The area of the anode in the solution, or in other words the current density at the anode, has considerable influence on the amount of activity. With I cm. of anode immersed in a certain solution, current .44 ampere, the activity was such as to give an electrometer rate of 2.70 divisions per second; with 7 cm. immersed in a similar solution the rate given was 4.16.

Activity as Related to Duration of Electrolysis and Current Strength. — As was expected the ratio of the activity of an anode to the time it has been used in electrolysis is nearly constant, when that time is not so long as to produce a noticeable effect on the power of the solution to deposit radioactive matter. Anodes were used in the electrolysis of a 500 c.c. thorium nitrate solution for various time intervals. The ratio of the activity to the time ran as follows:

Time of Blectrolysis. 2 minutes.		Ratio Activity of Anode to Time. .83
4	"	1.00
6	"	1.05
8	"	1.04
10	"	1.01
12	" "	1.05
14	66	1.11
16	" "	1.11

The relation between the current density and the amount of radioactivity on the anode is seen from the following results : The reason for the decreasing efficiency of the stronger currents is no doubt due to the nitric acid becoming so concentrated at the anode that the deposition of the brown coating was hindered to some extent. If very heavy current densities were used the brown deposit was sometimes redissolved.

Current Density at Anode, Amperes per cm <sup>2</sup> .	Ratio Current Density to Activity.
.017	1.00
.037	.89
.085	.87
.132	.69

With a voltage across the electrolytic cell just below that required to liberate oxygen and hydrogen at the electrodes lead peroxide is not deposited and the amount of radioactive matter of any kind deposited on the anode is small. From a solution of 5 gm. thorium nitrate no visible deposit was obtained in three hours, and the anode when tested showed no radioactivity.

Since thorium oxide is all the time giving off an emanation which causes secondary radioactivity, the following experiment was tried. 6.5 gm. thorium oxide was ground fine in a mortar and shaken up with 100 c.c. water. This water, with the thorium oxide still present in it, was subjected to electrolysis for twenty minutes, current .44 ampere. No radioactivity could be detected on either the anode or kathode. This is in accord with the results of Rutherford,<sup>1</sup> who finds that the emanating power of thorium, and therefore its power of imparting secondary activity to the surface of bodies in the neighborhood is at a maximum when it is in solution.

The Oxygen and Hydrogen from Electrolysis. — The oxygen and hydrogen liberated in the electrolysis of a solution of 20 gm. thorium nitrate in 300 c.c. water were collected separately in tubes above the electrodes and led at will into a testing cylinder, on the way passing through plugs of glass wool and a calcium chloride drying tube. The testing vessel consisted of a cylinder of brass 21 cm. long, 6 cm. in diameter, closed at each end with a plug of hard rubber. Through a hole in one plug the gas was led in from the drying tube, while a hole in the other allowed it to escape after traversing the length of the cylinder. A brass rod fixed to one of the hardrubber plugs passed down the middle of the cylinder nearly to the other end. This rod was connected to the electrometer and the cylinder to a source of potential, usually 280 volts. The current between the cylinder and central rod, as given by the electrometer rate, was taken as a measure of the radioactivity of the gas.

The volume of the collecting and drying tubes and connections was 95 c.c., so with a current of .84 amp. through the solution, giving .106 c.c. hydrogen per second, it took the gas so long to get from the electrode to the testing vessel that the radioactive matter present had lost nearly all its activity, and the electrometer rate was very small. When the current was increased to3.2 amp., giving .403 c.c. hydrogen per second, and the hydrogen led into the

<sup>1</sup> Phil. Mag., April, 1903.

testing vessel, the electrometer rate became steady in about fifteen minutes at 2.40 divisions per second. As soon as the hydrogen tube was disconnected the current began to decrease in the manner indicated by the following figures.

Нy	Hydrogen from Electrolysis of Thorium Nitrate Solution in Testing Vessel.						
Hye	irog	en flowing at rate of .403 c.c. per sec.,	2.40	elec.	divs.	per	sec.
45	sec.	after hydrogen flow was stopped,	1.60	"	"	"	"
60	"	later,	.80	"	**	64	**
120	"	66	.18	**	" "	"	**

Thus the rate of decrease of activity is about half in sixty seconds, or the same as that observed for the ordinary emanation from thorium, which is doubtless the radioactive matter present in the hydrogen.

When the oxygen was lead into the testing vessel, the same current flowing as above, giving .202 c.c. oxygen per second, a steady electrometer rate was attained in a few minutes. Results similar to those given above for hydrogen were obtained.

Oxygen from Electrolysis of Thorium Nitrate in Testing Vessel.

Оху	ger	flowing at the rate of .202 c.c. per second,	8.6	elec.	div	s. pe	r sec.
20 :	sec.	after oxygen flow was stopped,	7.5	**	**	" "	**
60	**	later,	3.7				
60	" "	<b>6</b> 6	1.9				

The rate of decay is the same as in the case of the hydrogen. The amount of activity measured would have been less than half that in the case of the hydrogen even if the concentration of the radioactive emanation were the same in the two gases when first liberated, since it took the oxygen twice as long to get from the electrode to the testing vessel and the activity of the emanation was decreasing in the meanwhile.

To decide the question of whether the radioactive matter was present in the same contentration in the two gases when first coming up from the solution the current was reduced to half so as to give the same rate of flow of hydrogen as of oxygen in the experiment above, and the hydrogen again led into the testing vessel. Now the steady rate attained was 7.5 electrometer divisions, or 12 per cent. less than with the same rate of flow of oxygen. The current was then decreased to .84 amp. and the electrolysis continued.



After 3 hours the current was again increased to 3.2 amp. and the hydrogen led into the testing vessel. The electrometer rate became steady at 15.1 divisions per second, as against 24.0 divisions when the electrolysis was first begun. This decreasing amount of the radioactive emanation in the gas as the electrolysis proceeds is sufficient to account for the difference in the concentration of the radioactive matter in the two gases, since the electrolysis had been continued for thirty minutes between the time of the measurements on the oxygen and those on the hydrogen. It is therefore probable that the concentration of the radioactive matter in the two gases is the same when they first leave the solution.

Electrolysis of Very Pure Thorium Solutions. — A 100 c.c. solution of (5 g. of) especially purified thorium nitrate which I was able to obtain through the kindness of Professor Baskerville was subjected to electrolysis for 20 minutes with a current of .84 ampere. No deposit was visible on the anode or kathode. The anode when tested for radioactivity gave an electrometer rate of 6.2 divisions per second. It was left in the testing vessel and 12 hours later was found to have practically no radioactivity. This was rather surprising, as an anode from the de Haen thorium nitrate would have lost only a little over half its activity in this time. The solution was again subjected to electrolysis under the same conditions and the anode afterwards tested at intervals with the following results:

		node from the Pure Thorium N	litrate Solution (	Baskervil	le).			
Immediately after the electrolysis.			5.4 electrometer divs. per					
75	minute	es later.	2.5	"	" "	"	"	
70	"	66	1.1	"	" "	"	"	
183	**	" "	.6	"	"	"	**	
121		66	.3	"	"	""	"	

From this it appears that the rate of decay of the secondary radioactivity excited by thorium is not a definite quantity. The rate indicated above is about half in one hour, the rate heretofore observed half in about eleven hours. The same solution was again subjected to  $e_{lowf}$  Jysis and a repetition of the results obtained.

thorium, such deposit possesses a temporary radioactivity. A few milligrams of copper nitrate were added to a solution of 5 gm. thorium nitrate in 100 c.c. water and a current sent through the solution, the current density being adjusted to give a bright adherent deposit of copper on the kathode. The voltage across the cell was 1.8. A clean but very thin coating of copper was obtained in five minutes and the activity of the copper coated kathode then tested.

Kathode Coated with Electrolytic Copper from a Thorium Solution.

5 m	inute	s after end of electrolysis.	2.62 electrometer divs. per sec		
3	**	later.	2.42		
3	**	66	1.82		
6	**	<b>6</b> 1	.83		
2	**	4.6	.58		
7	"	**	.14		
200	**	<b>66</b>	.00		

Here the rate of decay is even more rapid than in the case of the anodes from the pure thorium nitrate, though the source of the activity is the same thorium salt which gives an anode deposit, the activity of which decays at the rate of one half its value in eleven hours.

To get a deposit of oxide on the anode . I gm. of lead nitrate was added to a 100 c.c. solution of 5 gm. thorium nitrate, and the solution subjected to electrolysis for 15 minutes with a voltage of 2.10 across the cell. A thin adherent coating of lead oxide was obtained on the anode. The following results show the amount of its radioactivity and its rate of decay.

#### Anode Coated with Lead Oxide Deposited from a Thorium Solution.

3 1	ninute	es after electrolysis.	8.5 electrometer divs. per sec.
1	" "	later.	6.8
3	""	"	4.0
4	**	66	2.5
7	" "	<b>66</b>	1.8
32	**	<b>66</b>	.6

This is another example of rapid decay of the secondary activity from thorium.

Precipitates from Thorium Solutions. — Precipitates formed chemically in a solution with thorium nitrate present are radioactive. Silver chloride being a convenient precipitate to handle, tests were made of the rate of decay of its activity. About .1 gm. silver nitrate was added to a solution of 5 gm. thorium nitrate in 100 c.c. water. After the silver had been in the solution ten minutes it was precipitated out with the requisite amount of HCl, excess of acid being avoided. The precipitate of silver chloride was filtered out, dried over a waterbath, transferred to a small metal disc, and this set on the top of the central rod in the usual testing vessel. Measurements were taken at intervals.

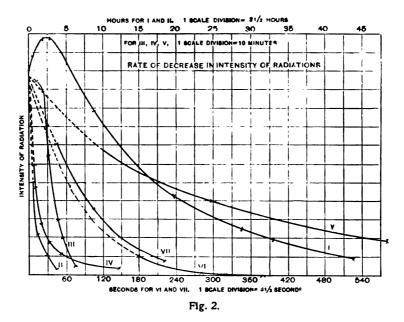
	Silver Chloride Precipitated from a Solution Containing Thorium.						
8.	5 minute	es after precipitation.	26.8 electrometer divs. per sec.				
30	"	later.	19.0				
60	"	66	. 11.0				
95	"	"	4.5				

A further study of such radioactive precipitates will doubtless prove of interest. One experiment relating to the effect of the precipitation on the radioactive properties of the solution itself was tried. About I gm. silver nitrate was added to a solution of 5 gm. thorium nitrate in 100 c.c. water and then the silver precipitated out with HCl. The solution was immediately subjected to electrolysis for five minutes with a current of .84 amp. and the activity of the anode tested.

Anode from Solution of Thorium Nitrate in which Silver Chloride had been Precipitated,						
180 seconds after end of electrolysis.			7.4 electrometer divs. per sec.			
100	) "	later.	1.1			
40	) "	**	.4			
60	) "	"	.1			
60	) "	66	.0			

Then a similar solution of thorium nitrate without the addition of the silver salt and HCl was electrolyzed, after .5 c.c.  $HNO_3$  had been added to make the amount of free acid in the solution at least as great as in the other solution. The activity of the anode after five minutes' electrolysis, current .84 ampere was such as to give an electrometer rate of 8.0 div. per. sec., with the usual rate of decay for the activity of the anode deposit from this de Haen thorium nitrate.

The rates of decrease with the time in intensity of the radiations from the various secondarily active substances obtained from thorium solutions is shown graphically in Fig. 2 by the curves, which are plotted, as far as possible, so that the ordinates, representing intensities of radiation, are the same at the start, that is, immediately after the electrolysis or precipitation. Curve I is plotted for the radiation from the lead peroxide deposit, and it is to be noted that its intensity increases at first in the same way as has been observed by Rutherford for the radiation from bodies made secondarily active by the thorium emanation, then it decreases in a geometrical pro-



gression with the time, falling to half value in about eleven hours. If  $I_0$  is the intensity at the beginning, and I the intensity at a time t later, we have  $I = I_0 e^{-\alpha t}$ , in which  $\alpha$  may be determined from the fact that  $I = \frac{1}{2}I_0$  when t = 11 hours. This decrease in approximately a geometrical progression with the time seems pretty general with secondary radioactivity. Curve II is plotted from the figures already given for the radiation from an anode after use in a very pure thorium nitrate solution, its decrease being about half in sixty minutes; III is for the radiation from copper deposited from a thorium nitrate solution, decrease half in seventy-five minutes; IV for that of lead oxide deposited similarly, decrease at first half in about sixty minutes; V for that of the silver chloride precipitated in



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a thorium solution, decrease half in eighty minutes; VI for that of the anode used in such a solution after the silver was precipitated, decrease half in forty seconds; and VII for that of the active matter in the hydrogen from the electrolysis of a thorium nitrate solution, decrease half in one minute.

Summary. — In the electrolysis of solutions of the thorium nitrate prepared by de Haen, of Hanover, a deposit of lead peroxide is obtained on the anode, and this deposit is highly radioactive at first. The intensity of its radiations increases slightly for about two hours, then decreases, falling to half value in about eleven hours. The radiations consist chiefly, if not wholly, of the non-penetrating  $\alpha$  type of radiations, with the exception that a small amount of radioactive gas similar to or identical with the thorium emanation is given off. The kathode has no secondarily active matter deposited on it.

The gases liberated in the electrolysis of a thorium nitrate solution are charged with radioactive matter, doubtless the ordinary emanation from thorium, which loses its activity at the rate of half in about one minute.

From solutions of the purest thorium nitrate obtainable no visible deposit is obtained on the anode, yet it is radioactive. The activity in this case decays rapidly, about half in one hour.

Anode and kathode deposits of oxides or metals from a solution containing thorium are radioactive. Their activity rapidly decreases, falling to half in a few minutes.

Precipitates thrown down chemically from solutions containing thorium nitrate are radioactive. Their activity also decays rapidly.

The secondary activity caused by thorium is not always the same in its rate of decay with time. The rate depends on how the secondarily active matter is separated from the thorium.

Coming to the question of the nature of the radioactivity shown by electrolytic and chemical deposits from thorium solutions, the lead peroxide, for example, two views are in general possible. First that the molecules or atoms of the lead peroxide have been so disturbed by being closely associated with the radioactive thorium that they now exhibit the properties of radioactive matter, or second, the radioactivity is a property of some kind of matter derived from the thorium which in some way becomes closely attached to the lead peroxide. The second view of secondary radioactivity is strongly supported by most of the work relating to the question. Adopting it there is still the question of how the radioactive matter comes to be so closely connected to the lead peroxide as to be precipitated with it, is the connection an atomic, molecular, or simply mechanical one; and how does it come to exert an influence varying with circumstances on the rate of decay of activity of the radioactive matter? Experiments on the relation between the length of time the lead is present in the thorium solution and the amount of active matter it collects, also of the rate decay of the activity, easily suggest themselves and some of them at least would have been performed and the results given here, had not circumstances prevented the further use of the apparatus until the fall. We should expect no essential difference between the secondarily radioactive deposits obtained electrolytically and those obtained chemically, for the forces involved are of the same nature.



## ON AN UNDESCRIBED FORM OF RADIATION.

#### FERNANDO SANFORD.

WHEN the terminals of the secondary winding of an induction coil are connected to the plates of an air condenser, the condenser plate connected to the kathode gives off a peculiar form of radiation into the condenser field whenever the current is interrupted in the primary coil. If a spark is allowed to pass between the discharging knobs of the secondary the radiation is given off from both condenser plates, but when no discharge occurs it is given off only from the kathode plate.

This radiation appears to the writer to be of the same nature as the ultra-violet radiation from a luminous body, and may be reflected, refracted and polarized as ordinary light. When it falls upon bodies placed in the condenser field these bodies become sources of a secondary radiation very similar in its properties to the primary radiation by which it is produced. This secondary radiation may, in the case of metals, at least, be given off both from the side of the body upon which the primary radiation from the kathode falls and from the side facing the anode. It may even be given off into an insulated hollow conductor placed in the condenser field.

In addition to this secondary radiation, the metals may reflect the original primary radiation.

Discovery. — This radiation was first observed by the present writer in 1892, and the observation was published in an article entitled "Some Experiments in Electric Photography" in the PHYSICAL REVIEW, Vol. II, p. 59, 1894. At that time some photographs were published which had been made by making a coin one of the plates of a condenser attached to the terminals of a very small induction coil, capable of giving a spark of only 2 or 3 mm. These photographs represented very clearly the relief figures of the coin, and one of them was made from a coin insulated F. SANFORD.

from the photographic plate by a thin sheet of mica. Attention was called to the fact that negatives had been thus made with the coin insulated from the photographic plate by paraffin, shellac and gutta percha, even through several millimeters of gutta percha, and the photographic effect was attributed to electro-magnetic waves sent off from the coin.

This explanation seems to have been unsatisfactory to all the physicists who have since written upon the subject, and the reduction of the silver salt has generally been attributed to the impingement'upon the sensitized film of electrified air particles driven off from the charged coin or to negatively charged electrons projected from the coin.

In an article entitled "Patterns produced by Charged Conductors on Sensitive Plates" published in *Nature*, Vol. 55, p. 485, March 25, 1897, I called attention to the fact that negatives had been made of coins imbedded in the center of a block of paraffin 2 cm. thick when the paraffin block and coin were laid upon the sensitive plate in a box which was placed in an alternating condenser field and carefully insulated from the condenser plates by heavy sheets of plate glass. This seemed to me at the time conclusive evidence that the photographs were not made by streams of electrified matter sent off from the charged coin. The same article was accompanied by a coin photograph made with the coin carefully insulated from the condenser plates by panes of plate glass, and from the sensitive plate by a sheet of mica, but the photograph was not published with the article.

In an article in *Nature*, Vol. 65, p. 400, February 27, 1902, Sir William Crookes refers to the experiments just mentioned and says : "Electrons will easily pass through paraffin wax from the coin to the sensitive plate when the coin is connected with the negative pole of an induction coil, the other pole being connected with a metal plate placed below the wax block." This assumes that the photographic effects which had been attributed by the present writer to

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plates of an alternating current condenser, no matter what the insulating material between them, since these photographs had been produced through all the best known insulators.

For the purpose of definitely settling the question whether the above described phenomena were due to a form of radiation or to a discharge of electrons, the experiments about to be described were carried on during the academic year just closed.

Method of Experimentation. — The experiments described below were made with a large induction coil and with a potential difference at the terminals of the secondary capable of giving a spark from 5 cm. to 15 cm. long when the condenser was connected across the terminals. An increase of this potential difference seemed to produce no other effect than to make the radiation more intense, and since this merely shortened the time of exposure of the sensitive plate while it made the necessary insulation more difficult, a potential difference capable of giving sparks from 6 cm. to 8 cm. long was generally used.

The primary current was broken by a rotating interrupter provided with a magnetic blow-out and driven by a motor at a speed which gave about ten interruptions a second, though the speed was varied through a considerable range without affecting the results. Various forms of condenser were used without any appreciable diference in the production of the radiation, but the condenser used in most of the experiments was made by pasting sheets of tin-foil about 10 cm. square on panes of glass about 30 cm. square and 5 mm. thick. In most of the experiments the plates were separated about 10 cm.

Various forms of camera, from a common black paper envelope to a tightly closed tin box, were used for holding the sensitive plate while in the condenser field, but the one most frequently used was made by fitting an old plate holder of a  $5 \times 7$ -camera to the top of a cigar box, so that the box could be closed by pushing in the hard rubber slide of the plate holder.

In exposing the sensitive plate to the radiation the condenser plate connected to the anode was usually supported horizontally with the tin foil below, the box camera was set upon the glass plate and the kathode plate was laid glass downward upon the box. The box containing the sensitive plate was thus insulated from both condenser plates.

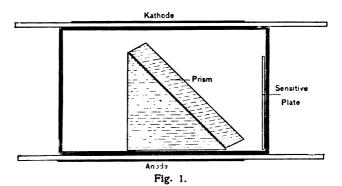
In some of the experiments hard rubber plates 6 mm. thick were used as insulators instead of the glass plates, but with no appreciable difference in the results.

Source of the Radiation .- In all the experiments previously described the photographs had been made while a discharge was taking place across a spark gap between the terminals of the secondary coil to which the condenser plates were attached. In the present experiments it was found that the radiation was more intense when no spark was allowed to pass, but that in this case it was given off only from the kathode plate, while in the other case it was given off from both plates. To compare the intensity of the radiation from the two condenser plates, two sensitive plates were cut from the same large plate, were placed back to back in a card-board box midway between the two sides of the box and held in position by wooden stops on both sides. The box was then placed on edge midway between two vertical condenser plates so that one sensitive plate would face each plate of the condenser. After the exposure, the plates were developed together for the same length of time. The plate facing the kathode was strongly blackened, while the one facing the anode remained clear. The blackening of the plate is accordingly due to something given off from the kathode.

When the kathode consists of a metal plate with only air between it and the sensitive plate there can be no question as to the source of the radiation, for in the case where the kathode is a coin the photograph shows clearly all the relief on the surface of the coin. When the kathode is a tin-foil sheet on glass or hard rubber there may be a question as to whether the radiation is derived from the metal or the insulating plate. Substances which are fairly opaque to the radiation when at a distance from the kathode may give it off profusely when in contact with the kathode. In experiments which No. 6.]

slide with the zinc or copper kathode laid upon it. In these cases the radiation was considerably more intense from the bare metal plate, but when an ordinary *papier maché* slide was used and tin foil placed upon it for a kathode the radiation was apparantly quite as intense as when a window was cut through the slide and the plate exposed directly to the tin foil. Since all of the insulating substances used are found to be more or less transparent to the radiation after it has left the kathode, it seems probable that the principal source of the radiation is in all cases at the face of the metal kathode.

Reflected and Secondary Radiation. — When the radiation from the condenser kathode falls upon other bodies a secondary radiation is given off from these bodies, and in the case of metals, at least, a



part of the primary radiation is reflected. In the case of non-metallic bodies the secondary radiation seems to be given off only from the face upon which the primary radiation falls, while in the case of metals it is given off from both sides.

For the purpose of comparing the secondary and reflected radiation from different surfaces the arrangement shown in Fig. I was used. The sensitive plate was set on edge at one end of the box camera already described. In this position it was found not to be affected by the primary radiation from the kathode. In front of it was a triangular wooden block lying on one side and having one face inclined at an angle of  $45^{\circ}$  to both the condenser kathode and sensitive plate, A triangular glass prism was laid upon this face of the block dividing it into two halves facing the vertical halves of the sensitive plate at the end of the box. The face of the block exposed

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on each side of the prism was about 4 cm. by 7 cm. The glass prism served to shield a part of each end of the plate from the radiation from the opposite side of the prism. Negatives exposed in this way showed four separate areas rather clearly marked off from each other. Fig. 2 is from a negative made with a white visiting card on one side of the prism and a strip of red glass on the other side. As the picture here given is a positive the lighter parts are those

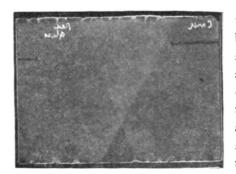
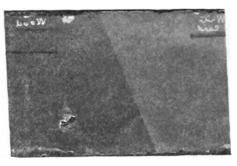


Fig. 2.

upon which the radiation was more intense. The black triangle at the bottom shows the part of the plate shielded from both sources of radiation by the end of the prism, the light triangular area above this shows the region illuminated by both sources and the medium dark areas on each side were each illumi-

nated by a single source. The shadows on each side were cast by pins which has been stuck in the sides of the box to hold the plate in position. It will be seen that the radiation was of nearly the

same intensity from each source, though a little stronger from the glass. Figure 3 shows a similar photograph made with the wooden block bare on one side of the prism and the white card laid upon the other side. In this case the intensity of the radiation from the





card is much greater than from the wood, but that from the wood was strong enough to show a distinct shadow of the pin.

In both photographs, as in all others made in this way, the dividing lines between the different areas are very sharp, and no sign of a penumbra can be observed. Since the source of radiation was in each case about 4 cm. wide, it is hard to explain this lack of penumbra. Apparently this secondary radiation is given off approximately normal to the surface of emission.

When a strip of sheet metal of any kind was placed on one side

of the prism the phenomenon became more complex. Fig. 4 is a photograph made from a strip of sheet aluminum on one side and the white card on the other side. In this case another rather clearly marked area appeared, as it did whenever any metal was used. This area, while showing clearly in the negative, is

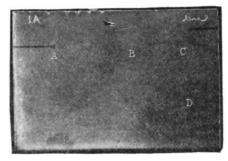


Fig. 4.

not brought out well in the photograph, and I have accordingly outlined it with dotted lines.

The metals accordingly seem to give off two kinds of radiation when the primary radiation falls upon them. One of these kinds gives the same sharply bounded shadow and inclined at the same angle as in the case of the secondary radiation from non-metallic bodies, while the other form bends much farther around the edge of the prism, as if it were sent off diffusely from all parts of the plate, though the gradual shading off in intensity which this should give is not perceptible in the negatives. Thus in the photograph given A is the area receiving both kinds of radiation from the aluminum, B the area receiving both kinds from the aluminum and the single kind from the card, C, the area receiving only the one kind from the aluminum and the radiation from the card, and D the area receiving radiation from the card only.

Presumably one of these forms of radiation is the primary radiation from the kathode reflected from the metal plate and the other is a secondary radiation induced at the surface upon which the primary radiation falls. Since non-metallic bodies give but the one kind, they are either reflectors of the primary radiation or sources of secondary radiation, but not both.

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### F. S.ANFORD.

The question as to which form of radiation from the metal surface is reflected and which is a secondary radiation was apparently settled as follows : Previous experiments had shown that metals, as coins, when placed in the alternating condenser field give off a radiation on the side opposite the kathode, hence this cannot be reflected radia-To compare this radiation with the two kinds given off from tion. the kathode side of the plate, the glass prism was fastened with wax to the lower side of a copper plate which was inclined at an angle of 45° with the kathode and the sensitive plate, which was laid on the bottom of the box. A white card was pasted to the copper plate on one side of the prism while the other side was left bare. The photographic plate was thus exposed only to the radiation from the side of the plate opposite to the kathode. The negative showed the same sharp shadows on both sides of the prism that were so plainly seen in Figs. 2 and 3, and indicated that the secondary radiation given off by the metal was the same as that given off by non-metallic substances. This experiment was repeated with a zinc plate on one side of the prism and a white card on the other side, and the result was the same as with the copper plate. This agrees with the well known fact that metals are much better reflectors for all forms of radiation than are the non-metallic bodies.

The relative intensities of the reflected and the secondary radiations from the kathode side of the metal plates was not accurately measured. In general, the plate seemed more than twice as dark where the two kinds of radiation fell upon it as it did where it was exposed only to the reflected radiation. All metals did not seem alike in this respect, but no quantitative comparisons were made. Gold leaf on glass seemed a proportionally better reflector than any of the other metals tested. No appreciable difference in the total radiation from two strips of the same metal could be observed when one was highly polished and the other considerably tarnished.

A number of non-metallic substances were tested with reference to their power of emitting the secondary radiation. Transparent glass was the poorest radiator tested and after it in their order came

#### FORM OF RADIATION.

The metals, in addition to their reflective power, are much better radiators than the non-metallic bodies. Very little difference could be observed in the radiative power of different metals. The metals tested were aluminum, copper, gold, iron, tjn, zinc and an amalgam mirror on glass. In the latter case the radiation had to pass through the glass, but it was apparently as strong as from the other metals. A lacquered iron ferrotype plate was compared with a piece of the same plate from which the lacquer had been polished off, and was appreciably poorer as a radiator than the polished iron. The difference in the quality of the secondary radiation from different metals will be discussed later.

The secondary radiation from the anode side of a metal plate is much weaker than from the kathode side. This was shown by supporting a plate of copper in the camera box at an angle of  $45^{\circ}$ to the condenser plates and placing one sensitive plate on the bottom

of the box and standing the other upright at the end of the box, both at the same distance from and inclined at the same angle to the copper plate. The result showed that the radiation from the kathode side was very much the stronger. The radiation from the anode side may, however, be strong enough to affect a photographic plate very quickly if the plate is placed near it.

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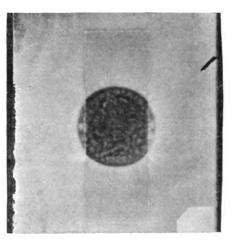


Fig. 5.

Fig. 5 is a photograph made from coin resting on a glass microscope slide which was laid upon the sensitive plate in the box camera and exposed to the primary radiation from the kathode. In this case, as in all the coin photographs made in this way, the raised parts of the coin are lighter, whereas if the radiation had penetrated the coin they should have been darker. This particular photograph also shows a distinction between the primary and secondary radiation.

The area outside the coin is illuminated by the primary radiation from the kathode. It will be seen that the glass slide is very transparent to this radiation. The coin projects beyond the glass on both sides, and the coin photograph below these parts is much lighter than under the glass showing that the secondary radiation from the coin was very considerably absorbed by the glass. The glass is accordingly more opaque to the secondary radiation from gold than to the primary radiation from the kathode. Similar differences will be shown later to hold between the secondary radiations from different metals.

Secondary Radiation in a Closed Hollow Conductor. — One interesting fact in regard to the secondary radiation from metals is that it may be given off inside a closed hollow conductor. Fig. 6 is a





photograph made on a plate which was placed in a tightly closed tin box and set inside the camera box. A piece of milkglass thermometer scale was laid on the film of the sensitive plate. The plate was exposed in the condenser field for five minutes. It had been previously observed that the milk-glass scale was

partly transparent to the radiation, while the ink of the scale was very opaque. This is shown in the photograph. The fact that the radiation penetrated the glass shows that the photograph was not due to the reducing effect of electrons from the sides of the box or the enclosed air.

Radiation from the Human Body. — When a sensitive plate was enclosed in a plate holder with hard rubber slides and laid in the condenser field and the hand was held upon the slide while the coil was being worked, the plate when developed showed a very black negative of the hand, showing that a very strong radiation was given out from the hand which was capable of penetrating hard rubber.

Regular Reflection. — Some attempts were made to focus the primary radiation by means of concave reflectors, but did not succeed. All the photographs which show a reflection of the primary radiation indicate that the reflection is largely diffuse. The fact that the best reflectors also give off a strong secondary radiation makes it difficult to determine to what extent the primary radiation is regularly reflected. In many of the experiments where a slit was used between the secondary radiators and the sensitive plate, images of the slit were formed by reflection from the cover of the box, especially when this cover was of red glass, as it was in some of the experiments. This showed conclusively that there was some regular reflection of either the primary or secondary radiation. This part of the subject needs much more investigation than I have yet been able to give it.

Refraction. --- Many experiments were performed on refraction with glass prisms and with hollow glass prisms filled with water, chloroform and other liquids. In general, these experiments were performed on the secondary and reflected radiation. Usually a strip of metal less than a centimeter wide was placed in the box at an angle of 45° with the kathode and a screen with a narrow vertical slit was placed about 5 cm. from the metal strip and between it and the sensitive plate, which was usually about 5 cm. from the slit. Sometimes two slits in line were used in order to secure the parallelism of the rays through the prism. With all the arrangements devised there were two images of the slit formed on the photographic plate. These images were always parallel, and were separated by greater or less distances according to the distance of the slit from the sensitive plate, being about 2 mm. or 3 mm. apart when the plate was 5 cm. from the slit. I am unable to explain the cause of this separation. The two images seem to be due to the two kinds of radiation, since when the metal strip was itself made the kathode only one image was formed. In some cases, also, the refraction was different for the two.

When a prism cut from a small spectacle lens was placed across a part of the slit the radiation which passed through the prism was refracted about four fifths as much as red light under the same conditions. When a flint-glass prism having a refracting angle of  $24^{\circ}$ was used the refractive index of the radiation from aluminum was found to be about n = 1.7. This is only a rough approximation.

When a hollow glass prism having a refracting angle of 14° was filled with water and placed before the slit it was seen that the two images of the slit were not equally displaced. One of the kinds of

radiation seemed to have a refractive index of about n = 1.4 and the other of n = 1.1. When filled with chloroform both refractive indices were nearly the same and were about n = 1.5. Later, it was found that the refractive index of the radiation may depend upon the nature of the metal which serves as its source. Several different metals were used as reflectors and the displacement of the slit images by a small crown-glass prism was determined, keeping all the conditions fixed except as to the metal reflector. In general, one image of the slit was displaced by about the same amount in all the experiments, while the other image was displaced more for some metals than for others. It was assumed that the image whose displacement was constant was due to the reflected primary radiation while the other was due to the secondary radiation sent off from the metal. When the photographic plate was at such a distance from the slit that the one image was displaced by about 2 mm., the other image was displaced as follows : For gold, 1.7 mm., tin, 2.8 mm., copper, 3 mm., aluminum, 4 mm. The displacement of the image produced by sunlight under the same conditions was 1.9 mm. A similar series of comparisons were afterward made with a flint-glass prism, and the differences in the refraction of the radiation from different metals were inappreciable. Differences in absorption corresponding with these differences in refraction are described later.

Total Reflection. — The slit images as described above were totally reflected by a right-angled prism so that they were formed at the side of the box, instead of directly in front of the slit. The radiation was also totally reflected when it was allowed to enter the base of a  $50^{\circ}$  prism and strike upon the face at an angle of  $25^{\circ}$ .

*Polarization.* — That the secondary and reflected radiation is not polarized when it leaves a copper plate was shown by passing it through two Nicols before it fell upon the photographic plate. The Nicols were placed side by side in the path of the radiation, but had their optic axes at right angles to each other. They seemed to transmit the radiation equally well.

The Nicols were then placed end to end with their optic axes parallel, and a plate was exposed for ten minutes to the radiation which might pass through them. Their axes were then crossed and No. 6.]

another plate cut from the same large plate was exposed for the same length of time, after which the two plates were developed together. The parallel Nicols allowed sufficient radiation to pass to give a very distinct image of their cross section, while the crossed Nicols quenched it completely.

Diffraction. — Many attempts were made to produce a diffraction spectrum by passing the radiation through gratings ruled on glass and by reflecting it from a metal grating. In the case of the glass gratings no diffraction could be observed. In one negative where an attempt was made to reflect an image of a slit from a Rowland grating a series of dark bands which looked like multiple images of the slit were formed on the plate but the plate was so strongly blackened by the secondary radiation and the diffusely reflected primary radiation that these images were not very distinct, and in several other negatives made as nearly as possible in the same way they could not be seen at all.

Attempts to produce interference bands by passing the radiation through a gypsum wedge between crossed Nicols were also unsuccessful.

Fluorescence. — When a tube of barium platinocyanide is placed in a strong alternating condenser field in a dark room the fluorescence of the tube may be plainly visible. To determine whether this florescence was due to the radiation in the condenser field, or to other causes, a glass tube of the cyanide was placed in the camera box near an upright sensitive plate and was exposed for several minutes to the radiation. No blackening due to fluorescence was visible when the plate was developed. A thin glass cell was then filled with the cyanide and placed directly against the sensitive plate and exposed to the radiation from a copper plate for several minutes. The salt served to screen the plate entirely from the action of the radiation, but showed no sign of fluorescence.

Absorption. — Both solids and liquids differ greatly in their transparency for both the primary and secondary radiation, and the same substance may differ in transparency for the secondary radiation from different sources. Most of the tests on transparency were made with the secondary and reflected radiation from a copper plate, though many were made with the direct radiation from copper, zinc and tin.

Of the solids tested, rock salt, quartz and glass, are the most transparent and their transparency is apparently in the order given above. Calcite is also very transparent, as is gypsum. Mica is much less transparent than glass and paraffin still more opaque. Colored minerals are usually less transparent than uncolored ones. Amethyst is fairly transparent, uranium glass less so, garnet still less and ruby and tourmaline very opaque. Ordinary red glass is very opaque, while the blue glass used in chemical laboratories is quite transparent. Cinnabar is fairly transparent, proustit is more opaque and zincite and rutil still more so. The metals are very opaque. A single layer of gold leaf or aluminum leaf seems to shut off the radiation completely. True, these give off a secondary radiation on the side opposite the kathode, but this is so weak as compared with the primary radiation which excites it, that if the photographic plate is placed at some distance from them they cast a complete shadow upon it. Some kinds of printing ink are very opaque. An aluminum advertising card laid upon a sensitive plate with the printed side next to the film, gave a negative on which the printing plainly appeared. The same phenomenon was shown in the photograph given in Fig. 6, where the printed scale is much more opaque than the milk-glass strip.

The metallic film deposited in a photographic negative is very opaque to the radiation, so that several positives were printed from negatives by its use. These positives differ but little, if at all, from those printed by sunlight. The intensity of the radiation was not great enough to print on sensitized paper, but the positives were made on glass plates which were exposed through the negative for several minutes and then developed.

In partially transparent substances, as in glass and mica, the absorption does not seem to be proportional to the thickness of the absorbing sheet. A glass cube 5 cm. thick showed but little more absorption than a glass microscope slide lying beside it. Several layers of mica sheets showed but little more absorption than a single sheet.

Absorption in Liquids. — The absorption of many liquids for the secondary and reflected radiation from a copper plate was tested by placing the liquids in a glass absorption cell about 1 cm. thick, which

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was placed directly before the sensitive plate. In general the liquids were compared with water by using a double absorption cell with water in one compartment and the liquid to be compared in the other. Many of the liquids tested seemed perfectly transparent, so that no more absorption could be observed when the cell was filled than when it was empty. In fact, in some cases the filled cell seemed more transparent than the empty cell. This was especially the case in a solution of salt and water. Probably in these cases the liquids and the glass had very nearly the same refractive index for the radiation, so that there was less reflection than in other cases.

The liquids tested may be classed under the three heads, transparent, partly transparent and opaque. They are given below in this arrangement:

Transparent.	Partly Transparent.	Opaque.
Water.	Potassic bromide in H <sub>2</sub> O.	Carbon disulphide.
Absolute alcohol.	Nickel sulphate "	Aniline.
Ether.	Copper " " "	Red ink (Carter's).
Chloroform.	Lead nitrate " "	Iodine in $H_{yO} + KBr$ .
Amyl alcohol.	Phenol pthyaline, red.	Iodine in alcohol.
Carbon tetrachloride.		Iodine in ether.
Ethyl acetate.		Potassic di-chromate.
Glycerine.		Nitro phenol in H <sub>2</sub> O.
Turpentine oil.	·	Copper chloride in H.O.
Toluene.		Copper chloride in HCl.
Iodine in chloroform.	+	Ferrous sulphate solution.
Ammonia.		PtCl, solution.
Sodium acetate solution.		Potassic ferricyanide solution
Mercuric chloride solution.		Potassic ferrocyanide "
Cadmium nitrate "	1	-
Ammonium sulphate "		
Potassic hydrate "		
Calcium chloride "		
Phenol pthyaline, solution.		

As in the case of light, the absorption of a substance in solution depends upon the nature of the compound formed in the solution rather than upon the nature of the dissolved substance or the solvent. Thus all the yellow solutions of iodine, though in transparent solvents, were quite opaque, while the red solution in chloroform was quite transparent. The colorless solution of phenol

pthyaline was quite transparent, while the red solution produced by adding a few drops of potassic hydrate solution was very opaque, though the potassic hydrate solution is itself very transparent. The difference in the photographic transparency of these solutions was greater than for light, as was shown by exposing one plate to light and another to the radiation through a double cell containing one solution in each side. The same difference was observed in other solutions, while carbon disulphide, which was optically perfectly transparent was very opaque to the radiation.

In some cases the absorption was very great for solutions of low concentration. A solution of platinum tetrachloride containing not more than one part by weight in two million parts of water was still appreciably opaque to the radiation from copper.

Differences in Secondary Radiation from Different Bodies. — For comparing the absorption of the secondary radiation from different substances the block inclined at an angle of  $45^{\circ}$  to the kathode and to the sensitive plate was used. A slit was sawn in the middle of the block and a triangular piece of red glass was set into it so that it stood with its vertical edge against the sensitive plate and prevented the radiation from one side of the glass from striking the

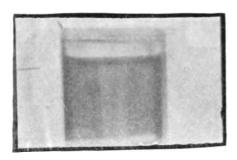


Fig. 7.

other side of the plate. When different substances were laid upon the block on opposite sides of the glass, their radiations were kept separate on the plate. A glass absorption cell about 1 cm. thick and with faces about 5 cm. square was placed against the photographic plate, the

block was moved so that the vertical edge of the glass partition came against the middle of one face of the cell and strips of the substances whose radiations were to be compared were laid upon the block. When the plate was developed after the exposure the photograph secured was as in Fig. 7. The dark vertical strip in the center shows the position of the glass partition. The light strip on each side of the center shows where the radiation from each side of the screen had lapped over onto the other side, and the darker strips outside of these show where each kind of radiation was absorbed by the liquid in the cell. In this particular photograph the absorption was nearly the same on both sides. The light horizontal strip above the liquid shows how much of the absorption was due to the glass.

The first comparisons were made in this way with a cell filled with a dilute solution of Carter's vermillion ink, which had been found very opaque to the radiation from copper. The substances used as sources of secondary radiation were wood, white paper, sealing wax, copper, tin, zinc, iron, aluminum and gold. The secondary radiation from the wood, paper and sealing wax was very completely absorbed. In the case of the radiations given off by the metals the absorption was greatest for the gold leaf and least for the iron. The differences between the other metals were inappreciable.

When the cell was filled with carbon disulphide the radiation from iron was absorbed least, that from aluminum came next, while that from copper, zinc, tin and a glass-amalgam mirror were about equally absorbed.

A dilute solution of  $PtCl_4$  was found to absorb the radiation from the different metals in the following order: zinc or aluminum, copper, iron, tin.

A piece of window glass was more transparent to the radiation from iron than from copper, and apparently slightly more transparent to the radiation from aluminum than from iron.

As is well known to any one who has attempted photometric work, the above comparisons are necessarily very rough, as no photographic method will enable one to measure accurately the relative intensities of two sources of illumination; but it is believed that they are in the right order.

Probable Nature of the Radiation.— As will be seen from the foregoing discussion, this radiation differs very materially in its properties from ordinary kathode radiation and not less so from the Roentgen radiation and the radiations so far described from the radioactive substances. It seems to approach much more nearly in its properties to ordinary ultra-violet light than do any of the others.

In fact, the most probable guess as to its wave-length would seem to place it in the ultra-violet only a short distance beyond the visible spectrum. Since alcohol is very transparent to it, while it is absorbed very strongly by carbon disulphide, its wave-length would seem to lie between 250  $\mu\mu$  and 400  $\mu\mu$ , and the fact that flint glass is very transparent to it would make it seem that its wave-length must be greater than 330  $\mu\mu$ . In all probability, the wave-length depends to some extent upon the character of the radiating surface. Thus the radiation from iron, being less absorbed by carbon disulphide than that from other metals tested, would seem to consist, in part at least, of greater wave-lengths than the others, probably about  $400 \mu\mu$ . It seems probable that waves of different length are sent off from the same metal. I do not yet despair of being able to measure the wave-length of the radiation from the different metals, though I have not yet been able to produce any interference effects. Of course, the possibility remains that the wave trains are too short to produce interference at sensible distances.

It has long been known that ultra-violet light may discharge negatively electrified metals, and it does not seem improbable that negatively electrified surfaces when suddenly charged and discharged may be capable of setting up a radiation of the same wavelength as that which is capable of causing their discharge. This makes it seem worth while to determine the particular wave-lengths which are capable of discharging different metals when negatively electrified.

Theory of the Radiation.— It is well known that if the experiments described had been carried on in the field of a condenser from which the air had been exhausted, the ordinary kathode radiation would have passed across from the kathode plate to the anode. Since this kathode radiation is believed to consist of negatively charged electrons driven off from the kathode, it seems probable that the same electrons will be sent off when the space between the condenser plates is filled with air. In the latter case, however, they would be stopped by colliding with air molecules before they had traveled far from the kathode, while in the former case they are stopped only by the anode or the walls of the containing vessel. No. 6.]

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These electrons, when striking against the walls of the tube or against a metal plate contained in the tube, give rise to the Roentgen radiation, and it seems probable that their collisions with the gas molecules in the condenser give rise to the radiation described in this paper.

STANFORD UNIVERSITY, June, 1903.

## ON THE THEORY OF THE COMPOUND PENDULUM.

## BY ROBERT R. TATNALL.

THE theory of the compound pendulum, considered as a rigid body making small oscillations, under gravity, about a fixed horizontal axis, is to be found in all treatises on dynamics; and the precautions and corrections which are necessary when such a body is to be used as an instrument of precision, have been carefully studied by Bessel, Helmert and many other investigators.

There is one aspect of the question, however, which, so far as I can discover, has nearly, if not quite, escaped notice, but which, by reason of its bearing upon the theory of the reversible pendulum, is not lacking in interest or importance. I refer to the case in which a definite portion of the oscillating body is movable with respect to the remaining portion. Or, in other words, the form of pendulum under discussion is that composed of two rigid masses, one of which carries the knife-edge, while the other may slide over the first, and be clamped to it at any desired point. The general problem, then, is to find how the period of the pendulum is affected by any specified change in the position of the movable mass.

I shall here consider only the special case in which the movable mass has its center of gravity always in the plane through the axis of rotation and the center of gravity of the first mass. This condition is realized in Kater's pendulum; it is also very approximately realized in clock pendulums regulated by a screw beneath the bob, but the latter are usually suspended by a flat spring, instead of a knife-edge, and so do not oscillate about a fixed axis.

While attempting to adjust a Kater pendulum belonging to this

period of the pendulum decreased until a minimum value was

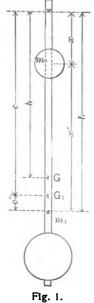
point near the knife-edge, was moved gradually downward, the

reached, after which it increased again. It is quite possible that this fact is already well known, but I have been thus far unable to find any discussion of it in the literature of dynamics. Probably no little confusion has resulted from the following erroneous, though somewhat popular, presentation of the compound pendulum idea. Suppose that a simple pendulum (bullet and thread), is suspended immediately in front of a compound pendulum, and from the same axis. If the length of the thread be equal to the distance from the axis to the center of oscillation of the compound pendulum, the latter will be unchanged in period by having the bullet attached to it. If the simple pendulum be lengthened, it will, by reason of increased period, and consequent tendency to lag in phase, retard the motion of the compound pendulum, when attached thereto, and so lengthen its period. On similar grounds it is frequently asserted that if the thread be shortened, instead of lengthened, the effect of consolidation will be to accelerate the compound pendulum, and shorten its period. This is equivalent to the assertion that if a compound pendulum be regarded as made up of an infinitude of material particles, then each particle which is farther from the axis than the center of oscillation will have a tendency to retard the pendulum, and so increase its period, while each particle which is nearer the axis than the center of oscillation will tend to diminish the period. That the last statement is erroneous may be easily seen. For if a particle of matter be added either at the axis, or at the center of oscillation, the period is not affected. But if it be added at any intermediate point, the period will be changed. Hence, if a particle be moved continuously from the axis to the center of oscillation, the period must pass through either a maximum or a minimum.

CONDITION FOR MINIMUM PERIOD.

In the case of the pendulum already described, one portion of which is adjustable along a vertical line through the center of gravity of the other, it is not difficult to determine the condition for minimum period, in terms of the constants of the two parts, and their

relative position. It is sufficient to find the condition that the length of equivalent simple pendulum shall be a minimum, since the period will be a minimum at the same time.



۱. م Let M be the mass of any pendulum, I its moment of inertia about the axis of suspension, and h the distance of the center of gravity from the axis. Then the length, l, of the equivalent simple pendulum is given by

$$l = \frac{I}{Mh}.$$
 (1)

In the pendulum represented in Fig. 1, the lower bob is rigidly attached to the rod carrying the knifeedge, these parts together constituting the "fixed" portion. The upper bob is the "movable" portion, and may be slid along the rod, and clamped at any point.  $G_1$  represents the center of gravity of the "fixed" portion, while G is the variable center of gravity of the entire pendulum. Further, let  $m_1 = \text{mass of "fixed" part,}$ 

 $m_2 = \text{mass of "movable" part,}$ 

 $M = m_1 + m_2 =$ total mass of pendulum,

 $I_1 =$ moment of inertia of "fixed" part,  $I_2 =$ moment of inertia of "movable" part,  $\}$  each about an axis

- through the c. g. of its own part, and parallel to the knifeedge,
- c = distance (constant) of c. g. of "fixed" part from the axis,
- x = distance of c. g. of "movable" part from the axis.

x and c will be taken positive when measured *downward* from the axis.

Then we have from equation (1), by the theorem of parallel axes, and by the definition of center of gravity,

$$l = \frac{I_1 + I_2 + m_1 c^2 + m_2 x^2}{m_1 c + m_2 x},$$
 (2)

which gives the length of equivalent simple pendulum, in terms of



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the distance of the movable mass from the axis. Equating to zero the differential coefficient of l with respect to x, we have, as the condition for a minimum (or maximum) value of l,

$$2x (m_1 c + m_2 x) - (m_1 c^2 + m_2 x^2 + I_1 + I_2) = 0,$$

which reduces to

$$m_2 x^2 + 2 m_1 c x - (m_1 c^2 + I_1 + I_2) = 0,$$

whence,

$$x = -\frac{m_1 c}{m_2} \pm \frac{1}{m_2} \sqrt{m_1 M c^2 + m_2 (I_1 + I_2)}.$$
 (3)

In the above quadratic in x, all the constants are essentially positive, while the constant term has a negative sign. Hence the roots given by equation (3) are always real and of opposite sign. Both values of x correspond to minima of l, and it is evident from equa-

tion (3) that these points are symmetrical about the point  $-\frac{m_1}{m_2}c$ , which is the position of the movable mass at which the value of l becomes infinite, since the moment about the axis here vanishes. The negative sense of the double sign in equation (3) therefore gives a large negative value of x, which brings the center of gravity of the pendulum above the axis; the pendulum then oscillating about the same axis in an inverted position. The positive sense of the double sign gives in all cases a positive value of x. Hence the following statement is perfectly general. In any compound pendulum, if a portion of the mass having its center of gravity initially in the axis of rotation, be moved continuously downward, the period will pass through a minimum value. In other words, the center of oscillation will first rise and then fall.

That this fact has not been clearly apprehended by writers on dynamics is evident from the following: Routh, Elementary Rigid Dynamics, 5th edition, Art. 93, Example 7. "\*\*\* If a heavy particle be attached to a vibrating pendulum, it follows that the period is increased or decreased according as the point of attachment is at a greater or less distance from the axis of suspension than the center of oscillation." For adding at any point a particle brought from outside the system is, as far as the effect on the period is concerned, exactly equivalent to sliding it to this point from either the axis or the center of oscillation.

R. R. TATNALL.

Further, it may be shown that the period reaches its minimum value when the distance of the center of gravity of the movable mass from the axis is one half the length of the equivalent simple pendulum.<sup>1</sup> This may be seen by substituting in equation (2) the values of x given by equation (3). The former equation will then reduce to

$$l=2x$$
.

The length of equivalent simple pendulum, expressed as a function of the distance of the movable mass from the axis, is of the form (see equation (2))

$$l=\frac{m+nx^2}{p+qx},$$

in which m, n, p, q are real constants. To find the condition that a function of this form may have a maximum or minimum value for some positive value of x, we have

$$\frac{dl}{dx} = \frac{2nx(p+qx) - q(m+nx^2)}{(p+qx)^2} = 0,$$

or

$$x = -\frac{p}{q} \pm \sqrt{\frac{p^2}{q^2} + \frac{m}{n}}.$$

In order that x may have a real and positive value, it is necessary and sufficient that the constants shall be finite, and that m and nshall have the same sign. This condition is evidently fulfilled in equation (2). Hence, the period of a compound pendulum will *always* pass through a maximum or minimum as x increases from zero. This positive value of x corresponds to a *minimum* and not a *maximum* in the case of the compound pendulum. For the value of  $d^2l/dx^2$  is found to be, after reduction,

$$\frac{d^2l}{dx^2} = 2 \frac{np^3 + np^2qx + mpq^2 + mq^3x}{(p+qx)^4},$$

<sup>1</sup> For a special case see Love : Theoretical Mechanics, Art. 224, Example 3.

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which is a positive quantity for positive values of x, in the case of the pendulum.

## Application to the Reversible Pendulum.

If the pendulum is provided with a second knife-edge, vertically below the first, and at distance b from it (see Fig. 1), then if b be such that the second knife-edge is below the center of gravity of the system, the pendulum may oscillate in an inverted position, about the second knife-edge.

Condition for Minimum Period for the Inverted Pendulum. — By analogy with equation (2), we may write the length of simple pendulum equivalent to this "inverted" pendulum in the form

$$l' = \frac{I_1 + I_2 + m_1 c'^2 + m_2 x'^2}{m_1 c' + m_2 x'},$$

where c' and x' are measured downward from the axis. But since c' = b - c, and x' = b - x, we have, in terms of x,

$$l' = \frac{I_1 + I_2 + m_1(b-c)^2 + m_2(b-x)^2}{m_1(b-c) + m_2(b-x)}.$$
 (4)

Equating to zero the differential coefficient of l' with respect to x, the condition for minimum period is found to be

$$x = \frac{Mb - m_1c}{m_2} \pm \frac{1}{m_2} \sqrt{(Mb - m_1c)^2 + m_2(m_1c^2 - Mb^2 + I_1 + I_2)},$$
(5)

where, as in the case of the "erect" pendulum, the positive sense of the double sign is to be used in practical cases. The possibility of imaginary values of x may here be accounted for by the necessity of imposing a condition upon the constants in equation (4), in order to insure that the center of gravity of the system shall lie between the two knife-edges. Otherwise, the pendulum cannot, of course, be made reversible.

Condition for Reciprocal Axes. — Kater's reversible pendulum derives its usefulness from the fact that if the position of the movable mass be so chosen that the periods about the two knifeedges are equal, the distance between these knife-edges is then equal to the length of the equivalent simple pendulum. The two axes of rotation are then said to be "reciprocal."

The condition that the axes shall be reciprocal is, therefore,

$$l=l'=b.$$

Substituting b for l' in equation (4), and solving for x, we obtain for the position of the movable bob,

$$x = \frac{b}{2} \pm \sqrt{\frac{b^2}{4} - \frac{1}{m_2} \{I_1 + I_2 - m_1 c(b-c)\}},$$
 (6)

b being the distance between the two knife-edges. There are therefore two positions of the center of gravity of the movable bob which will give equal periods about the two axes, and these positions, when real, are symmetrically situated with respect to the two knife-edges. These may be termed the two "reciprocal positions" of the adjustable bob.

Experimental Verification. — In order to verify experimentally some of the preceding results, the constants of the Kater pendulum of this laboratory were measured with sufficient accuracy, the distance c being measured from the axis about which the pendulum swung when erect, *i. e.*, with the heavy end down. The constants as determined were

$$m_1 = 3.915$$
 grams.  $I_1 = 5.950 \times 10^6$  C.G.S. units.  
 $m_2 = 676$  grams.  $I_2 = 0.008 \times 10^6$  " "   
 $c = 78.9$  cm.  $b = 96.7$  cm.

On substituting these values in equation (3), we obtain

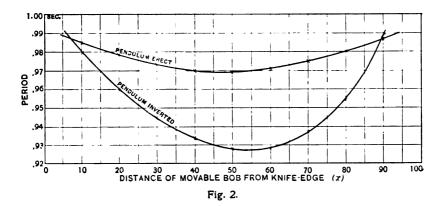
$x = \begin{cases} 46.7 \text{ cm.} \\ -961.1 \text{ "} \end{cases}$	(Positions of movable bob for
	{ minimum period; pendu-
	lum "erect."

x being measured downward from the axis of suspension to the center of gravity of the movable bob. As previously noted, the negative value of x corresponds to an inverted position of the pendulum, which does not occur in practice.

Similarly, by substitution in equation (5), one finds

$$x = \begin{cases} 53.9 \text{ cm.} \\ 345.7 \text{ "} \end{cases}$$
 Positions of movable bob for minimum period; pendulum "inverted."

The periods corresponding to various positions of the movable bob were then observed for both "erect" and "inverted" pendulum, by coincidences with a standard pendulum, and these are exhibited in the accompanying curves. The computed minima agree well with the minima of the curves.



Further, substitution of the constants in equation (6) gives for the two positions of the movable bob at which the period is unchanged by reversal of the pendulum,

$$x = \begin{cases} 7.6 \text{ cm.} \\ 89.1 \text{ cm.} \end{cases} \begin{cases} \text{Positions of movable bob for} \\ \text{reciprocal axes.} \\ (\text{Reciprocal positions.}) \end{cases}$$

At these two points the curve for the inverted pendulum and that for the erect pendulum should intersect; and the two points of intersection should have equal ordinates, since they correspond to equal periods. The curves are seen to conform sufficiently well to these requirements.

In the directions given by Stewart and Gee<sup>1</sup> for carrying out the adjustments of a reversible pendulum, it is stated that in order to obtain equality of periods, the adjustable bob is to be "always

<sup>1</sup> Practical Physics, Vol. I., p. 253.

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moved toward that knife-edge about which the time of oscillation is the greater." It will be clear, however, from the foregoing considerations, that this statement is at best incomplete, and may be quite incorrect; because if it be true for the *upper* reciprocal position in any pendulum, it must of necessity be untrue for the *lower* one (as shown by the curves, Fig. 2); and if true in respect to an upper reciprocal position when this is *below* the axis, it must be untrue for this position when *above* the axis. Indeed, no instructions of this kind can be given, except in special cases where the reciprocal positions of the adjustable bob are approximately known beforehand.

General Statement of the Effect of a Movable Bob. — The behavior of a reversible pendulum provided with a movable bob may be summarized as follows: When the center of gravity of the movable bob is at its upper reciprocal position, the center of oscillation of the pendulum is at the lower knife-edge. If the movable bob be continuously lowered, the center of oscillation continuously rises, reaching a maximum height when its distance from the center of gravity of the movable bob is equal to the distance of the latter from the axis. When the center of gravity of the movable bob reaches a position as far below the mid-point between the knife-edges as it initially was above this point, the center of oscillation is again at the lower knife-edge. After this, it continues to fall indefinitely.

Northwestern University, Evanston, Ill., October 1, 1903.



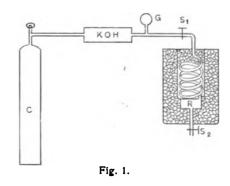
# THE HEAT OF VAPORIZATION OF OXYGEN, NITROGEN AND AIR.

#### By J. S. SHEARER.

I N a recent determination of the heat of vaporization of air<sup>1</sup> it was observed that the results varied in a fairly definite way with the change of composition of the liquid. It seemed desirable to determine this constant for each of the constituents in order that a comparison could be made of the heat required to vaporize corresponding amounts of oxygen and nitrogen when separate and when mixed as liquid air.

The apparatus used was described in the former paper and the only changes found desirable were to use manganin wire instead of german silver, as the latter becomes very brittle after several immersions in liquid air, and to use a chronograph to record the times when meter readings were taken. The gases were liquefied

by using liquid air as a cooling agent and subjecting the cold gas to considerable pressure. The apparatus used is shown in Fig. 1. Compressed gas from the cylinder Cpassed through an iron tube filled with caustic potash and then through a coil of fine copper tubing into a receptacle R. A gauge G indicates the drop



in pressure due to condensation, and when the pressure became constant the coil and receptacle were known to be filled with liquid. On closing stopcock  $S_1$  and opening  $S_2$  the liquid could be removed without wasting gas from the cylinder. This operation was repeated

<sup>1</sup> PHYSICAL REVIEW, Sept., 1902.

until the pressure in C became so low that further liquefaction was impossible. Oxygen liquefied very rapidly at pressures between 40 and 200 pounds per square inch but higher pressures are needed for nitrogen. A more economical method would be to use much greater pressures with small cylinders which could be entirely immersed in liquid air.

The oxygen was secured by electrolysis of water and after passing through caustic potash was found by analysis to be 98.8 to 99.9 per cent. pure. Atmospheric nitrogen was separated from oxygen by drawing air through iron tubes filled with copper turnings and heated above a red heat. The tubes used were two inches in diameter and about twenty inches long joined so as to make a rectangular coil giving approximately seventeen feet of copper packing. About 200 liters of nitrogen per hour was developed containing less than .5 per cent. oxygen. After filling the receiving reservoir, coal gas was passed through the hot coil, reducing the copper oxide, thus keeping up the activity of the copper.

The rate of vaporization was very constant when using the pure liquids even when considerable heat was developed by the coil, but when using liquid air there was a tendency to superheating and the meter readings were less regular. It is probable that the gas given off somewhat explosively when the current was used contained a larger quantity of nitrogen than that given off just before or just after this occurrence. Both of these facts tend to make it more difficult to get concordant results with liquid air than with the pure liquids.

A sample set of data for each gas may be of some interest.

Liquid Oxygen. December 19. 1902	2.	
Duration of run,	828	sec.
Loss rate (no current) I liter in	76	sec.
Total amount of gas registered by meter,	45	liters.
Net amount due to energy from current,	34.1	liters.
Mean temperature of gas at meter,	16.3°	с.
Mean value of current,	1.22	amperes.
Mean potential difference at terminals of heating coil,	10.97	volts.
Barometric pressure,	74	cm. Hg.
Density of oxygen at 0° —76 cm. Hg,	1.429	gm. per liter.
Variation of voltage during run,	.02	volt.
Heat of vaporization,	59.5	(minimum).

Second run,	63.0 (maximum).	
Mean of all six runs,	61.0	
Thermodynamic computation,	60.8	

The variation in the determinations of the temperature coefficient of vapor pressure is from 70 to 80, a much higher percentage than in the results of the heat of vaporization.

Nitrogen. March 27,	1903.
Duration of run,	<b>309.6</b> sec.
Time to lose I liter (no current),	135.0 sec.
Total register by meter,	30.0 liters.
Net vaporization due to current,	27.71 liters.
Average current,	1.54 amperes.
Average voltage,	13.61 volts
Average temperature,	21.5° C.
Barometer,	73.7 cm. Hg.
Density of nitrogen (grams per liter),	1.427
Heat of vaporization,	49.73 calories per gram.

Another run required 308.2 seconds to vaporize 30 liters as against 309.6 above. The mean value found from a series of similar observations was 49.83; the greatest variation from the mean was .11. The result agrees very well with that computed from the vapor tension, which gives 49.25.

The composition of the vapor given off was found by pyrogallol The following convenient method was used to deterabsorption. mine the corresponding liquid composition. The analysis of the liquid and vapor phases have been given by Baly and by Linde who allowed small portions of the liquid to vaporize completely in order to determine the liquid phase. If however readings of the meter are taken at small intervals from the start until all the liquid is vaporized and the vapor given off at each meter reading is analyzed a curve may be plotted using percentages of oxygen as ordinates and total amount of gas developed as abscissæ. The area of this curve gives the total oxygen content of the original liquid. The amount of oxygen in the liquid at any point is the area between the curve, the x axis, the ordinate at that point and the final ordinate. The composition of the liquid may thus be determined without in any way disturbing the process of vaporization. The results are given in the curves (Fig. 2). A comparison between the observed results and those computed assuming that the heat used for each component is

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Per Cent. O.	Heat of Vaporization Observed.	Heat of Vaporization Computed.
48	50.6	54
66.5	57.9	56.8
90	59	59.8

## TABLE I.

Curves I and II.

Per Cent. O Vapor.	Liters Evaporated.	Per Cent. O Liquid Computed.	Per Cent. O Vapor.	Liters Evaporated.	Per Cent. O Liquid Computed.
16.8	0	44.3	79	472	91.8
18.9	100	50	91.4	520	96.3
25	216	59	95.5	543	97.8
31.5	278	65.3	98	560.5	98.9
44.5	347	73.8		580.1(final).	
61	419	83.5			

# TABLE II.

Curves III and IV.

Per Cent. O Vapor.	Per Cent. O Liquid.	Per Cent. Total Gas.	Abs. T. [Baly].
16.8	44.3	0	80.7
17.5	47.3	10	81.0
19.5	51.0	20	81.3
22.2	55.1	30	81.7
26.1	61.5	40	82.4
33.3	66.6	50	83.5
44.6	73.8	60	85.1
58.0	81.5	70	86.7
77.0	91.0	80	88.8
91.9	96.2	90	90.2
		100	90.6

# TABLE III.<sup>1</sup>

Curve IV.

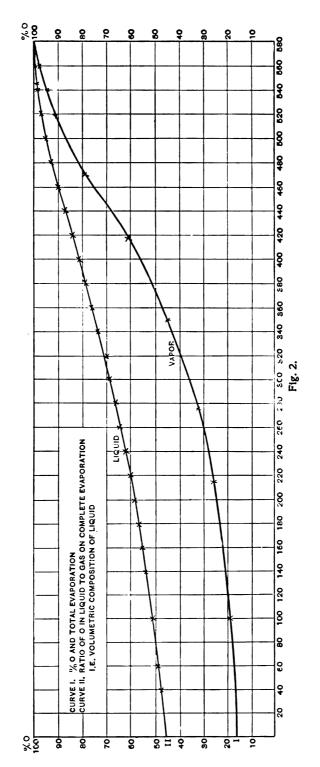
Т. АЬ. Т.С.	Per Cent. O Vapor.	Т. АЬ. Т.С.	Per Cent. O Vapor
80-193	12	86-187	52.3
81–192	17.6	87–18 <del>6</del>	60.3
82-191	24	88-185	69.5
83-190	30	89-184	79.2
84-189	36.8	90-183	89.6
85-188	44.4	91-182	

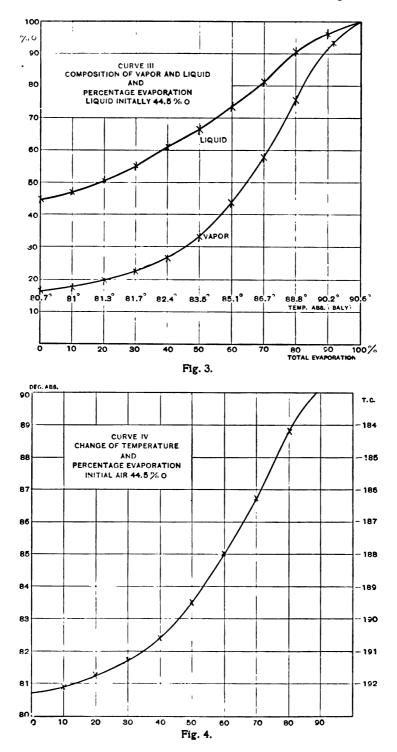
Boiling point of O 90.6°A. - 182.4°C.

"<sup>•</sup>" " N 77.5° — 195.5°C.

<sup>1</sup> Baly, Phil. Mag., 49, 217. Also Traver's Study of Gases.

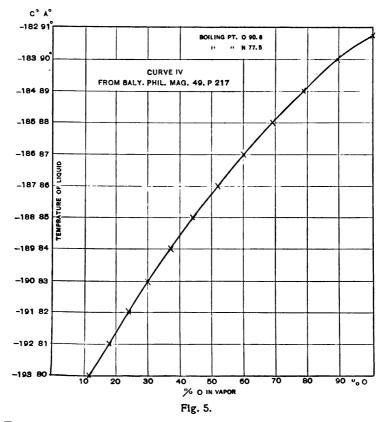
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the same as would be required to vaporize the same amount from the pure liquids is shown below. The agreement is not very exact but is as close as could be expected owing to the difficulties noted above.



For convenience in reference curves are added showing the variation in temperature with percentage of entire liquid evaporated. The values of the temperatures for various compositions of the vapor phase were taken from Baly.<sup>1</sup>

PHYSICAL LABORATORY, CORNELL UNIVERSITY, August, 1903.

<sup>1</sup> Phil. Mag. (49), p. 417, 1900.

# THE SPECTRAL ENERGY CURVE OF A BLACK BODY AT ROOM TEMPERATURE.

## BY G. W. STEWART.

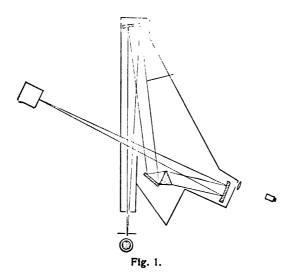
I N the past ten years much attention has been devoted to the study of the emission of solid bodies. An excellent résumé of the experimental and theoretical researches of Paschen, Lummer, Pringsheim, Wanner, Rubens, Kurlbaum, Wien, Rayleigh and Planck, is found in Vol. II. of Kayser's "Handbuch der Spectroscopie."

The measurements of the distribution of energy in the spectrum of a black body have been made with temperatures varying from about 1800° abs. to 373° abs. Langley <sup>1</sup> thought he obtained data for the distribution of energy in the spectrum of a black body at  $-20^{\circ}$  C., and Mendenhall and Saunders <sup>2</sup> state that they found the energy curve of a black body at  $-90^{\circ}$  C. It will be shown presently that the interpretations of these results were incorrect.

Lummer and Pringsheim<sup>3</sup> obtained a small portion of the spectrum of a screen at room temperature, used during their experiments.

The apparatus hitherto employed in the spectral energy curve measurements of a black body has consisted of a mirror spectrometer and a bolometer. The black body was placed in front of the slit of the spectrometer, the emitted energy passing through the spectrometer system and forming a prismatic spectrum at the bolometer strip slit. The change of temperature of the bolometer strip was then due to the resulting exchange of energy between it and the black body, and if there were enough difference between the find the distribution of energy in the spectrum of a black body at the temperature of the room by this method, it would be necessary to make the temperature of the spectrometer and bolometer very much lower than that of the room.

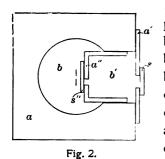
This being quite impracticable, a different device was adopted in the work here described. A radiometer and mirror spectrometer were kept at the temperature of the room, and the temperature of the black body was lowered to that of liquid air. In such an arrangement, since the deflections of the radiometer are proportional to the resulting exchange of energy, and since the energy emitted by the black body is very small in comparison, the deflection obtained is really proportional to the emission of the radiometer vane to the black body.



Langley and Mendenhall and Saunders failed to take this view of the matter. They seemed to think that their measurements gave them the distribution of energy in the spectrum of the black body, no matter what its temperature.

Apparatus and Adjustment. — The arrangement of the spectrometer and radiometer, Fig. 1, is practically the same as that described in a previous article.<sup>1</sup> The mirrors had a focal length of 55.7 cm. and <sup>1</sup>PHys. Rev., Vol. XIII., Nov., p. 257, 1901. an aperature of 9 cm. The mirror-prism device of Wadsworth <sup>1</sup> was used because the radiometer could be kept stationary, and because the radiation measured always passed through the prism at the angle of minimum deviation. The prism was of rock salt, and the refracting angle was  $59^{\circ} 47' 53''$ .

Fig. 2 is a horizontal cross-section of the radiometer. The instrument is the same as that used in previous work, cited above, save



a few modifications necessary for this particular experiment. a is the bronze block 5 cm.  $\times$  5 cm. with a vertical boring, b, 3 cm. in diameter; a' is a brass plate with a vertical slit soldered on the front of a horizontal boring b', 2 cm. in diameter; a'' is a brass tube with a vertical slit 2 mm. in width in its closed end, the tube being fitted in boring b'; s' and s'' are rock-salt plates;

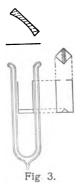
and in the center of b and in front of s'' are the vanes. Plate s' was used in order to obtain a vacuum, while s'' serves as a wall which is essential for a sensitive radiometric action.

The radiometer vanes were constructed to approach a perfectly black body as nearly as possible. Although the radiating vane is situated in a hole, yet its deflection depends not upon the total amount of energy radiated from the hole, but upon only the energy emitted by the vane. The vanes were made of platinum and coated with platinum-black. Kurlbaum<sup>2</sup> has shown that a coating of platinum-black, 200 gr. / dm.<sup>2</sup> at 100° C. emits about 97 per cent. of the radiation of an ideally black body at that temperature. In order to assure a thickness of at least 200 gr./dm.<sup>2</sup>, about four times this amount was deposited electrolytically according to Kurlbaum's method. While the vane emitted at least 97 per cent. as much energy as an ideally black body at 100° C., it does not follow that No. 6.]

The rotation of the radiometer vane was read by means of a telescope and scale.

Fig. 3 shows the apparatus which was placed in front of the spectrometer slit. The black body was an oblong tin box, with

top, heavily coated on the interior with lampblack. A V-shaped ridge was placed in the bottom in order to diminish direct reflection. This approximately black body was suspended in liquid air in a Dewar bulb, the latter being raised or lowered until the box just floated. The black body was thus kept at the same position. Above the bulb was placed a shutter made of glass and tin, and above this a concave mirror of about 11 cm. radius and 7 cm. aperture. The mirror, shutter and bulb were placed in front of the spectrometer slit, the distances being



such that the image of the slit of the black body fell upon the spectrometer slit. While this "black body" was not ideally black, yet, as will be shown, it was nearly enough so.

The prism table was first so adjusted that sodium light from the spectrometer slit passed through the prism at the angle of minimum deviation. The second mirror was then rotated so that the image of the spectrometer slit fell upon the radiometer slit, and the radiometer was at a known wave-length, that of the D-lines.

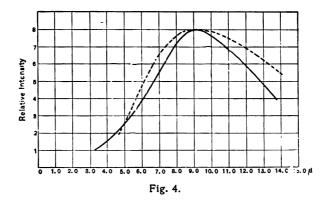
For observations in different parts of the spectrum, the prism table was rotated through an angle which was one half the change in minimum deviation.

Light striking the radiometer slit would be partly reflected from the rock-salt plate which was just behind. The lens shown near the second mirror in Fig. 1 was so adjusted that this reflected light fell upon it and was brought to a focus in the microscopic eye piece. By looking in the eye piece, the observer could determine when the image of the spectrometer coincided with the radiometer slit. This adjustment could be made by rotating the prism table to within 10''as read on the spectrometer, and 10'' error would mean less than .01 $\mu$  at any wave-length here considered.

The relative position of the vane and the radiometer slit was quite important, for the vane and slit were of the same width and if the vane were not directly behind the slit, the effective slit would be not only narrower, but displaced. This displacement would produce an error in the computed wave-length. In order to avoid this error, the vane was adjusted as correctly as possible with the eye, and then the apparatus was tested by finding the position of the  $CO_2$ emission band in an acetylene bunsen burner flame. If the maximum did not come at  $4.40\mu$  which is given by Paschen,<sup>1</sup> a leveling screw was turned until the vane was properly adjusted.

## RESULTS.

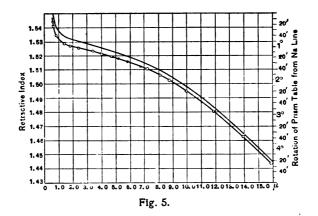
The distribution of energy in the spectrum of the approximately black body, the radiometer vane, was obtained by reading the deflections with the shutter open and closed. A number of observa-



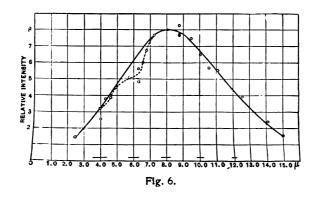
tions were taken for each setting of the prism table, and the average retained. These are the observed points in Fig. 4. The observed bands at  $4\mu$  to  $5\mu$  and  $6.2\mu$ , shown by a dotted line, are those of CO<sub>2</sub> and H<sub>2</sub>O respectively, the absorption being due to the gases occurring in the atmosphere of the room.

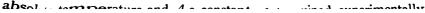
Paschen<sup>2</sup> states that the absorption bands of the CO<sub>2</sub> occur at about  $4.27\mu$ , and that there are a number of absorption bands of

accompanying Fig. 5, the lower curve is plotted with indices and wave-lengths as coördinates, and the upper curve gives the relation between the rotation of the prism table from the D-lines and the computed wave-lengths.



In Fig 6, the full line is the actual distribution of energy, the correction for slit width being made according to Paschen's <sup>1</sup> method. The maximum intensity occurs at  $9.2\mu$ . It is of interest to compare this maximum with that which would be predicted by the equation  $\lambda_m T = A$ ,  $\lambda_m$  being the wave-length of the maximum, T the





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Paschen's 'value is 2920, and Lummer and Pringsheim <sup>2</sup> have found 2940. The temperature of the room during the experiments here described was about 24° C., or 297° abs. Using the latter value for T and Paschen's value of A, the wave-length of the maximum becomes  $9.8\mu$ , which does not agree with that observed,  $9.2\mu$ .

There are several sources of error in the experimental work but, as will be seen, they do not seem to account for the difference between the predicted and observed position of the maximum. Neither the radiometer vane nor the box at liquid air temperature is an ideally black body. The latter does not need to be even an approximately black body for the maximum of its spectrum is at such a great distance from  $q\mu$  that its relative absorption in this region would be practically the same as that of a black body. As stated before, the vane was covered with platinum-black to such a thickness that it would at 100° C. emit more than 97 per cent. of the radiation of an ideally black body. The wave-length of the maximum emission at that temperature would be 7.8 $\mu$ , and hence the energy in the neighborhood of  $q\mu$  and  $10\mu$  would be a considerable portion of the entire energy. If the difference between the total emission of the vane and that of a black body, both at 100° C., is less than 3 per cent., and if this 3 per cent. error is distributed, and not in one region, then it seems quite impossible for the maximum of the emission of the vane at 24° C. to differ appreciably from the maximum of an ideally black body.

It is interesting to compare the results of these observations with a curve obtained from the equation of Planck. His equation is

$$J = c_1 \lambda^{-5} (e^{\lambda t} - 1)^{-1}.$$

Here J is the energy at any wave-length  $\lambda$ , T is the absolute temperature, and  $c_1$  and  $c_2$  are constants. The value  $c_2$  is, from theory, 4.965  $\times \lambda_m T$ . If, for the sake of comparison, the value for  $\lambda_m T$  found in this experiment be used,  $c_2$  becomes 13,530.

Using this constant, the relative values of  $J/c_1$  are plotted by a dotted curve in Fig. 6. As will be seen, the theoretical and experimental curves do not agree.

<sup>1</sup>Annal., 4, p. 277, 1901. <sup>2</sup> Verh. d. D. Phys. Gesell., 1, p. 215, 1899.



No. 6.]

While I am at a loss to understand why my results do not agree with those demanded by a well-verified theory, yet I do not urge them as any objection to the theory. The maximum deflection obtained was only about 4 mm. on a scale 64 cm. from the mirror, but the consistency of the results annuls any criticism on the basis of the minuteness of the deflections.

The experimental work was performed at the Physical Laboratory of Cornell University.

STATE UNIVERSITY OF NORTH DAKOTA, September, 1903.

## A CONVENIENT GALVANOMETER.

#### BY WALTER P. WHITE.

THIS instrument is the result of an attempt to design a galvanometer for elementary work. The requirements set were : that it should be reliable, accurate, quick-acting, direct reading, portable, and capable of being constructed in the humblest high school laboratory. The result seems to justify the expectation that the instrument may prove useful in advanced, as well as elementary, work. Comparing it with the Weston milammeters, it is at least as accurate, can be read as quickly and easily, and has the same resistance for a given sensibility. It has the disadvantage that its indifference to outside magnetic disturbances, though great, is not complete — on the other hand, it costs far less than a good commercial ammeter, and has other less fundamental advantages.

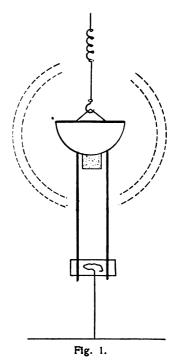
No one feature of the galvanometer is new - indeed, the combination is, in a general way, such as follows naturally from an application of the reflecting principle in a field where an adherence to the old-fashioned tangent galvanometer type with needle and pointer has effectually prevented the development of satisfactory instruments. The reflecting galvanometer, on account of the smaller deflection used and the greater radius of the scale, does not require so careful centering of the needle, and hence a simple instrument is in this respect as good as a very expensive galvanometer with a pointer. The short needle is more quick acting. The shortness of the needle and the smaller deflection combine to give a small displacement of the poles of the needle; the diameter of coil necessary to make the instrument obey the tangent law is thus very much' reduced, and from this fact follow several advantages. First, it becomes convenient to use a movable magnet system of two needles, with poles oppositely directed, such as are universally employed in sensitive astatic galvanometers. The fact seems to be often overlooked that

this arrangement is valuable for securing freedom from magnetic disturbances in less sensitive instruments also. The use of this kind of a magnet system, which by itself would be astatic, requires, of course, the addition of a control magnet. Second, the small coil renders it possible to make the resistance several hundred times as small, for the same sensibility. In practice, it is better to sacrifice some of this gain and make the coil more powerful, correspondingly increasing the magnetic control. In this way we keep the needle under the action of comparatively strong forces, and thus obtain a freedom from the action of convection air currents inside the case which is quite as important as freedom from magnetic disturbances.

Freedom from both magnetic and mechanical disturbances is thus promoted by the use of a control magnet. In addition, such

a magnet renders it very easy to regulate the sensibility of the galvanometer so that the reading is given directly in some accepted unit. A third advantage is that constancy which can be secured in a modern laboratory only by being independent of what is by courtesy called the earth's field. The ability, also, to use the instrument in any desired position regardless of the points of the compass is often a decided advantage. This advantage is limited, however, by the fact that the absolute sensitiveness varies by a fraction of one per cent. in different orientations.

For the magnet system the Weiss form has been selected, in which there are two vertical needles, each end of the combination having two unlike poles, belonging to different magnets, but acting like the two poles of a hori-



zontal magnet whose length is equal to the distance between the two needles. Such a system has practically permanent astaticism,

and is far easier to construct than the usual form, especially for a novice. The needles actually used are 1.2 mm. thick and 43 mm. long, placed 8 mm. apart (see Fig. 1). The weight is about a gram, which gives stability. The astaticism is so good that, with the control magnet producing a field equivalent to about eight times that of the earth exerted on each pole, the maximum disturbing effect of the actual earth's field usually causes a deviation of about fourteen minutes of arc. Better results might be obtained, for the assembling of each system took only two or three minutes, and consisted in laying the needles, as nearly parallel as could be judged by the eye, on two strips of mica, and fastening them there with sealing wax, applied with a warm nail. It would require, however, considerable skill and more patience to approach the above result by building up a system of the ordinarý type.

The damper is a horizontal wire, 4 cm. long, turning in a shallow layer of clean kerosene. Air and magnetic dampers are out of the question for portable galvanometers with fiber suspension, on account of the very small clearance required if they are to be effective. The damper here described, however, is more than a mere substitute — it is in many respects preferable even for stationary instruments. It is easier to make, never requires adjustment, is not disturbed by dust or displacements of the galvanometer, and suffers far less from convection currents than an air damper.

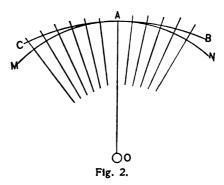
That the old fashioned type of tangent galvanometer has often been preferred to the cheaper, more accurate, and more efficient mirror galvanometer is, perhaps, mainly due to the following reasons: The slowness of the reflecting galvanometer when damped in the usual way; its greater sensitiveness to disturbances (when used in the "earth's field"), and the trouble that fiber suspensions give by breaking. It has just been shown that the two first considerations are altogether in favor of the mirror instrument, when it is properly made; the third difficulty has been avoided by hanging the suspension from a small spring, which weakens the effect of shocks, and by using a bundle of eight silk fibers instead of one.

#### No. 6.] A CONVENIENT GALVANOMETER.

its effect varies from that of an approximately equal amount of magnetic control, which determines the error in an empirically calibrated instrument.)

In order to make the galvanometer direct reading, the scale is bent to a curve such that distances measured along it are pro-

portional to the tangent of half the angle subtended. When a template has once been made it is as easy to make such scales as to make straight ones. A board can be sawed in two along the proper curve and then screwed together again, clamping one edge of a flexible scale in the cut. An error of as much as a



a millimeter in the saw cut causes an error in the scale readings which is inappreciable, even when the scale distance is only 25 cm. To obtain the proper curve, a circular arc, MAN, Fig. 2, is described with radius, OA, equal to the proposed scale distance; radii are drawn two degrees apart; these radii are extended beyond the circumference as follows:

					-
At 2	4 6	8	10 12	14	degrees from $A$
Add   .0002	.0008 .0021	.0036 .	.0055 .0085	.0108	of the radius.
At 16	18 20	22	24 28	1	degrees from A
Add0143	.0183 .0227	.0274	.0327 .0440		of the radius.
-	-				

A smooth curve, CAB, is drawn through the points thus located. The readings will be proportional to current with uniform scale divisions of any length. The zero must be at A, and the scale distance equal to OA.

These numbers were determined by triangulation, using six-place tables. Three different systems of triangulation gave concordant results.

The scale is read by the double mirror system. A small stationary mirror, either below and behind or above and in front of the

W. P. WHITE.

swinging one, gives an image of a line somewhere on the scale. If the mirror nearest the eye is thin, this line appears to come close up to the scale as seen in the other mirror, and thus serves as an index. Since the eye is in focus for both images at the same time, this arrangement dispenses with a telescope. At 25 cm. scale distance, divisions 2 mm. long can be read to tenths. A telescope is decidedly preferable, however, for those who have learned to use it without undue effort. With a telescope 13 cm. long one can with much greater ease read millimeter divisions, thus doubling the range of the instrument.

There are two coils, of the Helmholtz type, each 4 cm. in diameter. The ratio of magnet length to coil diameter is thus 1:5. With this ratio, and with each half of the scale subtending an angle of 28°, the greatest possible error due to irregularity of the field is about 1/2,000 of the length of the scale.<sup>1</sup> Fig. 1 shows the magnet system with suspending spring and fibers, hemispherical mirror, and damping wire, full size. The upper piece of mica is behind the mirror. The dotted circles show the size of the coils, and the small dotted square shows the position of the stationary mirror. For a sensibility of one milliampere there may well be twenty turns in the coils, which should have a resistance not over .1 ohm.

The writer has used one of these instruments for a great variety of work. Its coils have 160 turns, 3 ohms resistance, and the reading is in tenths of milliamperes, with shunts for milli- and centiamperes. A calibration showed no error greater than .001 the length of the scale. The instrument is not necessarily quite as accurate as this, since there may have been errors in reading, or in the standard resistances, greater than any observed — still, an in-

<sup>1</sup> Half this error is that inseparable from a perfect Helmholtz galvanometer, and the other half is the error which would result if the true distance of the coils were one millimeter in error. (There is an even chance that the two errors may oppose each other.) The unavoidable error varies approximately as the fourth power of the ratio of magnet length to coil diameter, the other, as the square of this ratio, and also as the square of the ratio of the error in distance to the coil diameter. Hence if the diameter of the coil is increased the gain in accuracy will be as the fourth power of the ratio of increase, but

strument whose inaccuracy can not be detected through the use of a good resistance box is good enough for many kinds of work. Even more gratifying than the accuracy, however, are the quickness and the certainty of the readings, which, in comparison with the generality of even excellent galvanometers, are very striking.

Most of the features above described are already familiar in other instruments, or are such that their advantages can be readily estimated. A fluid damper, however, seems often to be considered liable to cause large errors through surface tension effects.

Otherwise, such dampers would prove valuable --- they are practically indispensable in a portable reflecting galvanometer and would greatly improve many existing instruments, to which they could be easily applied. To test the magnitude of the surface tension effects. a magnet system was observed in which they were made 2,500 times as great as need be, by making the damper attachment very eccentric, and by moving the wall of the containing vessel to and fro through a space of 8 mm., which gives 64 times the variation of distance that would occur with a damper centered to within .5 mm. and turning through an angle of 14°. Not the slightest effect was observable in a telescope half a meter away. The magnet system weighed 40 gm., and its time of vibration was .25 second. Increasing the time to 10 seconds would make the system 1,600 times as sensitive to disturbances, but the substitution of a well-made damper would evidently more than offset this. We may say, then, that the surface effect may be made negligible for any magnet which is heavy enough to need such damping at all. The fluid in this case was ordinary kerosene, and the diameter of the containing vessel, 7 The necessary diameter can readily be found by trial in any cm. A horizontal wire is better than a vane, in that it particular case. allows the use of a very shallow layer of fluid. Convection currents are much smaller in such a layer, and waves, if any occur, are more quickly damped out.

CORNELL UNIVERSITY.

## NOTE.

### By J. E. TREVOR.

Josiah Willard Gibbs .- In the death of Professor Josiah Willard Gibbs, in April 1903, there passed away a man whose work has left a lasting impression on the course of the development of physical science. Gibbs's life was the quiet and outwardly uneventful one of The son of Josiah Willard Gibbs, the widely known phila scholar. ologist and Professor of Sacred Literature in the Yale Divinity School from 1824 to 1861, he was the sixth of the family bearing this name. His schooling was obtained in New Haven; and he was graduated from Yale College, where he won a number of undergraduate distinctions in Latin and Mathematics, with the class of 1858. After five years of graduate study at Yale he obtained the degree of Doctor of Philosophy, and then became a tutor in the college. In this capacity he taught Latin for two years and "Natural Philosophy" for one, and then went abroad for further study in physics and mathematics. The winter of 1866-67 he spent in Paris, the following winter and spring in Berlin, where Magnus then was, the third winter in Heidelberg under the influence of Kirchhoff and Helmholtz, and the succeeding spring again in France. Gibbs then returned home, and in 1871 was appointed Professor of Mathematical Physics in Yale College, which position he filled for the remainder of his life.

Gibbs's published researches in physics were in the fields of thermodynamics, the electromagnetic theory of light, and statistical mechanics; his work in pure mathematics was in vector analysis graphical representation. The ordinary pressure-volume diagram, in which areas represent quantities of work, the temperature-entropy diagram, in which they represent quantities of heat, and the volumeentropy diagram, among others, are discussed in a most interesting way. This study led naturally to the subject of the next paper, A Method of Geometrical Representation of the Thermodynamic Properties of Substances by means of Surfaces.<sup>1</sup> A thermodynamic surface, in which the coördinates are pressure, volume, and temperature, had been suggested by James Thomson; but Gibbs here describes a far more general one, the surface

$$\varepsilon = f(v, \eta),$$

in which  $\varepsilon$  is the energy, v the volume, and  $\eta$  the entropy of a body. This surface furnishes the only geometrical representation of *all* the stable and instable states of a body of constant composition: every other fails in some respect with the appearance of two-phase or three-phase states. Because of the differential equation

$$d\varepsilon = -pdv + td\eta,$$

the position of the tangent plane at any point of the surface represents the pressure and temperature corresponding to the point. After establishing in most ingenious fashion the criterion of equilibrium under imposed conditions of constant pressure and temperature, Gibbs is enabled to indicate the form of the analytical surface  $\varepsilon = f(v, \eta)$  throughout the entire range of stable and instable states; and thereupon to construct the "derived surfaces" that represent the possible multiphase states. The whole supplies a remarkably beautiful representation of the theory of the analytical continuity of the primitive one-phase state. This paper attracted Maxwell's attention to such a degree that he devoted a number of pages of his well-known Theory of Heat to an account of the surface; and he constructed a model of it, a cast of which was presented to Gibbs. A very interesting analytical exposition of the properties of Gibbs's energy surface has been recently given in a paper by Paul Saurel.<sup>2</sup>

> <sup>1</sup> Trans. Conn. Acad. 2, 382, 1873. <sup>2</sup> Jour. Phys. Chem. 6, 474, 1902.

These studies in the graphics of thermodynamics led naturally to the results of the epoch-making paper, On the Equilibrium of Heterogeneous Substances,<sup>1</sup> in which the criteria of thermodynamic equilibrium are applied to systems of bodies differing in chemical nature and even subject to reversible chemical interaction. This investigation is one of the most imposing results of the scientific activity of the nineteenth century, and is widely considered to be Gibbs's most important contribution to physical science. Its extent is tremendous; although compact to a degree, it occupies over three hundred closely printed pages, and contains seven hundred numbered equations.

Gibbs begins by showing that the fundamental criterion of thermodynamic equilibrium, that the entropy of a material system must be a maximum under imposed conditions of constant energy and volume, can be transformed into the analytically more serviceable theorem that equilibrium will subsist when the energy is a minimum under the conditions of constant volume and entropy. He then regards the energy of a homogeneous mass of variable composition as a function of the volume v of the mass, the entropy  $\eta$ , and the masses  $m_i$  of the independently variable components, thus establishing the equation

$$d\varepsilon = -pdv + tdr_1 + \mu_1 dm_1 + \mu_2 dm_2 + \dots + \mu_n dm_n,$$

in which p, t are the pressure and absolute temperature of the mass, and the quantities  $\mu_{i}$ , termed the "potentials" of the components, are defined as the mass derivatives of the energy. Influences due to gravity, distortion of the solid masses, capillary tensions, and electricity are temporarily neglected. Application of the criterion of equilibrium to a system of coexistent phases then yields the important general result that, for equilibrium, each potential must have the same value in all the phases.

Integration of the above differential equation under the supposition that the mass of the phase increases from zero to a finite value, its nature and state remaining unchanged, yields

$$\varepsilon - pv + t\eta = \mu_1 m_1 + \mu_2 m_2 + \dots + \mu_n m_n,$$

<sup>1</sup>Trans. Conn. Acad. 3, 108, 1896; 3, 343, 1878.



a relation which asserts that the thermodynamic potential of the phase is a linear function of the potentials of the components. It is then shown that, because of the form of the differential equation for  $\varepsilon$ , all the n + 3 independent relations between the 2n + 5 variables involved can be found by differentiation when the form of the function  $\varepsilon(v, \eta, m_1, m_2, \dots, m_n)$  is known. By analytical transformation of the differential equation, it is shown that the same result follows when the form of the free energy  $\psi(v, t, m_1, m_2, \dots, m_n)$ of the heat-function  $\chi(p, \eta, m_1, m_2, \dots, m_n)$ , of the thermody, namic potential  $\zeta(p, t, m_1, m_2, \dots, m_n)$ , or of a function  $f(p, t, \mu_1, \dots, m_n)$  $\mu_2, \dots, \mu_n$ ), is known. Gibbs terms the equations  $\varepsilon = \varphi(v, \eta, m_1, m_2, \dots, \mu_n)$  $\dots, m_{n}$ ), etc., "fundamental equations." This important demonstration, that the study of the thermodynamic properties of a phase is completed when the form of one of its fundamental equations is determined from experiment, is a generalization and extension of Massieu's theory of the "characteristic functions" of fluids.

Application of the equations to a system of r coexistent phases leads now to the famous "phase rule" — the conclusion that such a system is capable of but n + 2 - r independent variations of state. Elimination of differentials from the r phase-equations

$$0 = -vdp + \eta dt + m_1 d\mu_1 + m_2 d\mu_2 + \dots + m_n d\mu_n$$

then supplies for the ratios of the differentials dp, dt,  $d\mu_1$ ,  $\cdots$  expressions in terms of the volumes, entropies, and compositions of the several phases. In the case of the derivative dp/dt, these results constitute a most interesting generalization of the Clapeyron-Clausius equation.

Referring back to the paper on the energy surface for a onecomponent system, it is pointed out that such a geometrical representation is furnished by each of the surfaces

$$\begin{split} \varepsilon &= f_1(v, \eta, m) & \chi = f_3(p, \eta, m) \\ \psi &= f_2(v, t, m) & \zeta = f_4(p, t, m), \end{split}$$

these surfaces bearing definite relationships to one another, and the most comprehensive of them being the first. Gibbs then shows how the equation

$$\boldsymbol{\zeta} = f(\boldsymbol{p}, t, m_1, m_2, \cdots, m_n)$$

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can be employed for a representation, by means of families of surfaces, of the equilibria of two-component and three-component phase systems, an intricate matter which he develops in considerable suggestive detail. In all such applications of the theory Gibbs's introduction of fundamental equations has been very clarifying, giving unity to the subject and making clear what relations must be found from experiment to the end of making possible the complete integral treatment of thermodynamic problems by purely analytical means — in his phase, "giving shape to research."

The remainder of the first half of the paper, the part published in 1876, contains two applications of great interest. In a discussion of the values of the potentials when the quantity of one of the components is very small, Gibbs distinctly outlines the general features of the celebrated theory of dilute solutions formulated by van't Hoff ten years later, carrying the matter as far as was permitted by the experimental facts available at the time. The second application is the theory of dissociation of gases. The condition of dissociation-equilibrium is that the potentials of the proximate components of the gas mixture shall satisfy an equation of the same form as that obtaining between the units of weight of these components. This theory of dissociation was tested by assuming the components to obey the laws of ideal gases, and from the fundamental equations of such gases calculating the forms of the potentials of the components. The result was cast into the form of a relation between the density and the pressure and temperature of the mixture, and was found to exhibit a striking agreement with the existing determinations, made by Deville and Troost and by Playfair and Wanklyn, of the densities of nitrogen peroxide. This test was extended<sup>1</sup> in 1879 to a calculation of the "abnormal vapor densities" of formic and acetic acids and of phosphorus perchloride.

The second half of the paper, issued two years after the appearance of the first, commences with a deduction, from the general cri-

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the distinguishing feature of which is the inclusion of the term  $td\eta$  in the expression for the differential of the energy of the cell. A most interesting abstract of the whole paper, by its author, appeared in the sixteenth volume of the American Journal of Science.

The method of this paper, being an analytical development of the consequences of inductively established general postulates, is of great effectiveness, and it is applied with remarkable physical insight and mathematical skill. The significance and importance of the results attained were not at first realized; partly no doubt because of what has been called the "logical austerity" of the method, but certainly in considerable measure because the work appeared in a publication not generally accessible to scientific workers. Because the work remained for a long time virtually unknown, some of its results were rediscovered by others in later years. A striking instance of this was Helmholtz's celebrated development, in 1882, of the theory of free energy; which was essentially a development of the properties of Gibbs's function  $\psi$ .

Yet, now, a quarter of a century after their publication, Gibbs's results are powerfully influencing experimentalists and theoreticians alike. This is especially true of the phase rule, and of the theory of the critical states of systems of two or more independently variable components. The phase rule, to which attention was first directed by the Amsterdam physicist van der Waals, in the hands of Roozeboom and his followers, Schreinemakers, Bancroft, and others, has brought order into an apparently inextricable tangle of chemical and physical facts. One of the most extended single applications of it is van't Hoff's recent study of the very complex equilibria subsisting between the solid phases deposited in the evaporation of sea water; and the "rule" has of late shed much needed light on the operations of the manufacture of steel. Every recent treatise on thermodynamics bears evidence of the deeply modifying influence that Gibbs's work has exerted on the subject. The most extensive of these, Duhem's monumental work on "chemical mechanics," is essentially an exposition and development of Gibbs's theory.

A distinct service was rendered to contemporary physics and chemistry by Ostwald's publication, in 1892, of a German version '

<sup>1</sup> Thermodynamische Studien, Leipzig, 1892.

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of the three papers from the Transactions of the Connecticut Academy. This was followed, in 1899, by Le Chatelier's translation<sup>1</sup> of the first part of the "Equilibrium of Heterogeneous Substances." This paper in particular, as a scientific classic, must eventually be made generally accessible in English : we cannot indefinitely content ourselves with the not very readable German text and the incomplete French one. What is badly needed is a collected edition of all Gibbs's thermodynamic publications.

After the publication of these thermodynamic researches, Gibbs's creative scientific activity lay in the fields of multiple algebra and vector analysis, and in the electromagnetic theory of light and statistical mechanics. Feeling, with other physicists, the need of a simple and direct algebra of vectors, he developed such an analysis in which the product of two vectors is so formed as to give a positive value. This avoided the loss of naturalness in the Hamiltonian system of quaternions, due to the fact that it causes the square of a vector to become negative. A privately circulated outline of this vector analysis, issued in part in 1881 and completed in 1884, attracted considerable favorable attention, which interest has been transferred to the authorized systematic exposition of the theory prepared by Dr. E. B. Wilson two years ago. In the intervening years Gibbs developed a number of applications of the new analysis to problems of astronomy and physics, and made original contributions to the broader subject of multiple algebra in general.

Between 1882 and 1889, Gibbs published a series of papers on the electromagnetic theory of light, and its relations to the various elastic theories. By simple and direct methods, and with a notable absence of special hypotheses regarding a connection between matter and ether, he gave the first adequate explanation, on the basis of the theory, of the dispersion of colors, and developed a number of consequences concerning refraction and polarization. Of his arguments for excluding the theories of light other than the electrical, it has been said that "they would have sufficed to firmly establish this theory even if the experimental discoveries of Hertz

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No. 6. ]

In his Elementary Principles in Statistical Mechanics, published in 1902 as one of the Yale Bicentennial Publications, Gibbs returns to an aspect of the subject of his first researches - thermodynamics. In the endeavor to deduce the laws of thermodynamics from the principles of mechanics, Clausius, Maxwell, and Boltzmann, among others, were led to study the approximate and probable behavior of systems of so great a number of particles that we have not the fineness of perception to enable us to appreciate quantities of the order of magnitude of those that relate to a single particle. To the end of placing such "statistical" inquiries on a firm and certain foundation, Gibbs undertook a general development of the subject. In his own words: "We may imagine a great number of systems of the same nature, but differing in the configurations and velocities which they have at a given instant, and differing not merely infinitesimally, but it may be so as to embrace every conceivable combination of configuration and velocities. And here we may set the problem, not to follow a particular system through its succession of configurations, but to determine how the whole number of systems will be distributed among the various conceivable configurations and velocities at any required time, when the distribution has been given for some one time." Following this programme, the work is primarily an exposition of the methods that must be used in developing this particular branch of the mechanics of conservative systems. The attempt to utilize the results for the establishment of a mechanical theory of thermodynamics is given a distinctly secondary place, and Gibbs utters the wholesome warning that "it should be distinctly stated that, if the results obtained when the numbers of degrees of freedom are enormous coincide sensibly with the general laws of thermodynamics, however interesting and significant this coincidence may be, we are still far from having explained the phenomena of nature with respect to these laws. . . . The phenomena of radiant heat, which certainly should not be neglected in any complete system of thermodynamics, and the electrical phenomena associated with the combination of atoms, seem to show that the hypothesis of systems of a finite number of degrees of freedom is inadequate for the explanation of the properties of bodies."

In the development of his researches, Gibbs worked systemati-

cally and alone. He rarely spoke of a piece of work until it was completed, even refusing at times to say what he was engaged upon at the moment. This was a manifestation of his characteristic unassuming manner and retiring disposition. On one occasion a distinguished French man of science, who had come to New Haven to see Gibbs, called upon him in company with a colleague from one of the language departments who had volunteered to act as interpreter. Gibbs politely accepted the service, and only after a half hour's struggle of the interpreter with unfamiliar technical terms could the embarrassed man bring himself to the admission that he spoke French. Gibbs's lectures were carefully prepared and enriched with a wealth of concrete illustrations, and he held himself always ready to extend help to those who sought it of him, either in person or through correspondence. Academic honors came to him in great number. In 1881 he was the Rumford medalist of the American Academy, and ten years later the Copley medalist of the Royal Society. Four honorary degrees were conferred upon him by American and foreign universities, and he was a member of some fifteen academies and learned societies. A list of his published papers may be found in the American Journal of Science for September, 1903.



# PROCEEDINGS

# OF THE

# American Physical Society.

# MINUTES OF THE TWENTY-FIRST MEETING.

A REGULAR meeting of the Physical Society was held in Fayerweather Hall, Columbia University, New York City, on Saturday, October 31, 1903, President Webster being in the chair.

The following papers were presented :

1. The Distribution of Motion in a Conducting Gas. P. G. NUTTING.

2. On the Nature of Certain Radiations from the Sulphate of Quinine. FANNY COOK GATES.

3. Phenomena of Imparted Radioactivity. W. J. HAMMER.

4. The Van der Waals a in alcohol and ether. EDWIN H. HALL.

5. On the Misuse of Physics by Biologists and Engineers. W. S. FRANKLIN.

6. Mechanical Rotation Produced by the Electrodeless Discharge. (Exhibition of apparatus.) BERGEN DAVIS.

7. Theory of the Electrodeless Discharge. BERGEN DAVIS.

# ON THE NATURE OF CERTAIN RADIATIONS FROM THE SULPHATE OF OUININE.<sup>1</sup>

BY FANNY COOK GATES.

WHEN the sulphate of quinine is either heated or cooled through a high range of temperature, it is known to become temporarily phosphorescent and to possess the power of discharging an electroscope.

It has been thought by some that this phenomenon, resulting from simple chemical reactions, is an argument for attributing the radiations of radium and the other active minerals to purely chemical changes. To obtain evidence in favor of or against such a view, experiments were

<sup>1</sup> Abstract of a paper presented at the meeting of the Physical Society held on October 31, 1903. THE AMERICAN PHYSICAL SOCIETY. [Vol. XVII.

made ascertaining the nature of the radiations given off by quinine sulphate under the conditions named, and a comparison made between their characteristic properties and those of the radiations from the radioactive substances.

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The quinine was sifted uniformly over a metal plate and heated to a known temperature, immediately after which it was placed in a testing vessel between parallel electrodes one of which was joined to the quadrants of an electrometer and the other to the pole of a storage battery, other connections being made as usual. Here it was allowed to cool to a known temperature and the total amount of radiation emitted by the quinine during a given change in temperature was measured by the quantity of electricity discharged through the electrometer. By changing the range and the rate of cooling and the strength and direction of the electric field, curves were obtained showing the exact effect of such variations on the resulting radiation. The absorption of the rays in air and in other substances was also tested.

Unlike the radiations from the radioactive substances, which are incapable of alteration through any change in temperature and appear not to vary with time, the radiations from quinine sulphate are only apparent when accompanied by a great change in temperature. They vary in intensity during this change and in a short time they cease altogether. By increasing the strength of the electric field it is impossible to secure a maximum ionization current from the quinine radiations although a saturation current is readily produced with the radiations from radium, thorium and uranium. The quinine radiations are completely absorbed by a very thin sheet of aluminum and are largely absorbed by two or three millimeters of air and probably by less, which is in marked contrast to even the least penetrating rays of the active elements. other striking difference in the behavior of the two types of rays is that those from quinine undergo a change in intensity when the direction of the field is changed. When the lower electrode on which the quinine rests is joined to the positive pole of the battery the resulting current is invariably larger than when it is joined to the negative pole.

The variation of the current with electromotive force is very similar to that obtained when ultra-violet light falls on a charged surface except that both positive and negative ions are present. The difficulty in obtaining saturation is doubtless caused by the fact that the ionization takes place very close to the surface of the quinine and that the ions rapidly diffuse to its The effect appears to be due to some type of radiation which is rapidly absorbed in the gas, and since the electrical effects are accompanied by marked phosphoresence it is possible that the ionization is caused by very short waves of ultra-violet light, such as Lenard has shown to be active in ionizing the gas.

These considerations give no evidence for believing that the ionization is due to projected bodies and make it appear certain that the ionizing action of quinine is caused by molecular actions which are influenced by temperature, and not by the spontaneous projection of charged masses from the atom, as in the case of radioactive bodies.

# THE THEORY OF THE ELECTRODELESS DISCHARGE.<sup>1</sup>

#### BY BERGEN DAVIS.

THE theory of the discharge developed is derived from and explains some direct experimental data on the number of volts per centimeter required to produce the electrodeless discharge in gases at various pressures.

The electrodeless discharge was produced by the discharge of a Leyden jar system, which system was charged by the secondary of an induction coil giving 180 discharges per second. The spark gap in the secondary was adjusted until the white discharge just appeared in the vessel.

The volts per centimeter acting around the vessel were directly measured by a coil of five turns of wire of a diameter slightly less than that of the vessel. This coil was connected to a micrometer spark gap. The coil that had produced the discharge was lowered over the coil, and the micrometer spark gap adjusted till a spark passed. The potential at this spark gap divided by the length of wire in the measuring coil gave the volts per centimeter acting around the vessel.

Two frequencies of oscillation of the Leyden jar system were used.

Let  $T_1$  and  $T_2$  be the time of a half oscillation for the two frequencies, then

$$T_1 = \frac{1}{28} \times 10^{-5} \text{ seconds.}$$
  
$$T_2 = \frac{1}{15} \times 10^{-5} \text{ seconds.}$$

The results obtained were as follows:

1. The volts pericentimeter required to produce the discharge depends on the nature of the gas.

2. There is a minimum potential for each gas. The minimum and the pressure at which it occurs depends on the frequency of oscillation.

<sup>1</sup>Abstract of a paper presented at the meeting of the Physical Society, held on October 31, 1903. 3. The volts per centimeter are dependent on the frequency of oscillation for all pressures below the critical pressure, but are independent of the frequency for pressures above the critical point.

4. The number of volts through which an ion must freely run to produce ionization by collision.

5. The ratio of the ionic to the molecular mean free path.

Experiments were made in air, carbon dioxide and helium. The potential gradients obtained for air are shown in curves in Figs. 1 and 2.

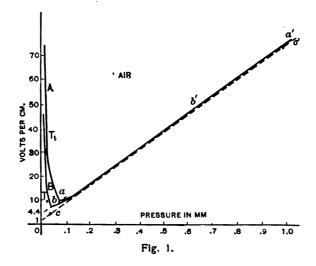


Fig. 2 is the part of the curves for pressures below the minimum shown on an enlarged scale.

#### THEORY OF THE DISCHARGE.

The curves for pressures above the critical are nearly straight lines. They have the equation

$$X = cp + d. \tag{1}$$

The curves of the pressures below the minimum are equilateral hyperbolas, having equation

$$X = \frac{\rho^{\rho} \sigma^{\nu}}{\rho}.$$
 (2)

The ionization is taken as due to impact of other ions. Consider that when the discharge appears, there are N ions present, and before the application of the force there are  $N_0$  ions in a unit volume of gas. Then during a half-oscillation the ionization builds up from  $N_0$  to N ions, according to the equation No. 6.]

$$N = N_0 e^{aa}.$$
 (3)

Where  $a = \log b$ , and b is the number of ions produced by one ion at each impact including itself. a is the number of successive impacts in T, the time of a half oscillation.

It is assumed that N and  $N_0$  vary in such way that  $N/N_0 = \text{constant}$  for any pressure, then aa = constant.

The mean path  $\lambda$  of an ion, will be traversed under a force X in time t according to

$$\lambda = \frac{1}{2} (X - V_0) \frac{\epsilon}{m} t^2$$
(4)

But a = T/t, since a is the number of times that the ions go through their free path in time T. Consequently:

$$X = \lambda \frac{2a^{2}m}{T^{2}e^{-}} + v_{0}.$$
 (5)

 $v_0$  in equations (4) and (5) represents the total amount of the electrical intensity that is consumed by the delay of the ions after each impact. This quantity  $v_0$  is found to vary inversely as the pressure, that is

 $v_0 = V\lambda$ .

Hence (5) becomes

$$X = \lambda \left( \frac{2a^2m}{T^2\bar{e}} + \mathcal{V} \right). \tag{6}$$

Equation (6) is the complete equation for the discharge at pressures below the critical pressure. The constant V is the displacement of the equilateral hyperbola along the axes of coördinates. It is the point of intersection of line (abg) in Fig. 2, with this axis. In air it has the value of 4.4 volts.

The electrical intensity at pressures above the minimum is independent of the frequency of oscillation. The condition to be satisfied is that the electrical intensity X shall be such that  $Xe\lambda$  is a constant and equal to w, the energy of ionization by impact.

The equation of the discharge at pressures above the critical pressure is

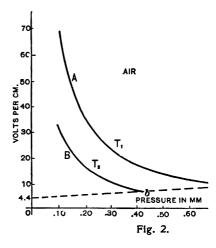
$$X_{n}\left[\frac{2}{\pi} + \frac{\pi - 2}{\pi}\sin\frac{\pi}{2}\sqrt{\frac{p - p_{0}}{p}}\right] = \frac{w}{\epsilon\lambda} + d. \tag{7}$$

The left member of this equation represents the departure of the observed curve from a right line. This departure is due to the fact that the The measuring instrument measured the potential. Hence

$$X = \frac{2}{\pi} X_{\mathbf{m}}.$$

At pressures above the critical point the co discharge is that  $Xe\lambda$  shall attain the value w. minimum (critical) point, the energy  $Xe\lambda$  excee The controlling condition here is that the ionia sity N for the appearance of the discharge. T the intersection of these two controlling condition

The constants, V and d in equations 6 and The method of finding V has been previously



d is the intersection of the asymptote to the cu dinates.

The mean free path of an ion at a given by solving equation (6) for two values of Xvalues of T. The two equations so obtained which is a constant for all pressures and freque

The results obtained for the three gases are gi

	v	d	א/אי	
Air.	4.4	1	4.4	

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V and d are constants previously explained.  $\lambda/\lambda'$  is the ratio of the mean free path of an ion to that of a molecule. The constant a is the number of successive impacts which the  $N_0$  ions make during the time of a half oscillation. P is the number of volts through which an ion must run to produce ions by collision.

The ionization is due to the impact of negative ions only. The positive ions, owing to their greater mass, run through only a small part of their mean free path in the time T, while on the other hand the negative ions make a successive impacts in the same time.

My thanks are due to Professor J. J. Thomson for his cordial advice and interest during the progress of this work at the Cavendish Laboratories. I wish also to acknowledge my obligations to the John Tyndall fellowship fund of Columbia University which made this work at the Cavendish Laboratories possible.

# NEW BOOKS.

# Light Waves and Their Uses. By A. A. MICHELSON. The University of Chicago Press, 1903.

This very welcome addition to our literature in applied optics is based on a series of lectures delivered in the spring of 1899 at the Lowell Institute. After a general statement of wave phenomena and interference, a chapter is devoted to a comparison of the relative efficiency of the microscope, telescope and interferometer for the measurement of small quantities. Then follows a discussion of the application of interference methods to measurements of distances and angles which gives a very clear statement of the methods and arrangement of mirrors best adapted for various purposes. In the lecture on spectroscopic investigations readers will be pleased to find an admirable presentation of the use of the "visibility" curve, a matter not, perhaps, generally understood.

The determination of the length of the standard meter in terms of the wave-length of certain definite radiations is a monument to the skill and patience of the author, and is here quite fully explained. A description of the eschelon grating and a lecture on astronomical applications is followed by a discussion of the ether and an account of experiments made in efforts to determine the relation of the ether to ordinary matter. While investigators in this field are by no means in agreement as to the interpretation of the results, yet the author points out substantial progress toward the solution of this complex problem.

The book is notable for the complete absence of mathematical expressions and for that peculiar attractiveness only found in the writings of actual investigators in their chosen field. No student interested in optical phenomena or their applications should fail to read these lectures with more than ordinary care.

J. S. SHEARER.

Storage Battery Engineering, A Practical Treatise for Engineers. By LAMAR LYNDON. New York, The McGraw Publishing Co., 1903. Pp. 382.

The purpose of this book is to aid engineers in the design and maintenance of storage battery equipments. The book is divided into two nearly equal parts. The first includes the construction and management of the lead storage battery, while the second part is devoted to a description of the methods in vogue for the application of accumulators to engineering practice.

The theory of the action of accumulators is touched very lightly. But the practical questions of the mechanical design of the cell and the care and management of battery installations are considered in detail. The most striking part of the book, however, is the excellent description of the various methods for using accumulators in connection with distribution and power work. In this connection much attention is given to the consideration of auxiliary apparatus and automatic regulating devices.

ERVIN S. FERRY.

A Calendar of Invention and Discovery. By JOHN CASSAN WAIT. New York, McGraw Publishing Co, 1903.

The subject matter of this calendar is varied and voluminous; scientific and biographical items of all kinds, commonly a dozen or more under one note, have been brought together and arranged in calendar form. The calendar will prove interesting to many, and occasionally valuable, for the miscellaneous contents have been well indexed.

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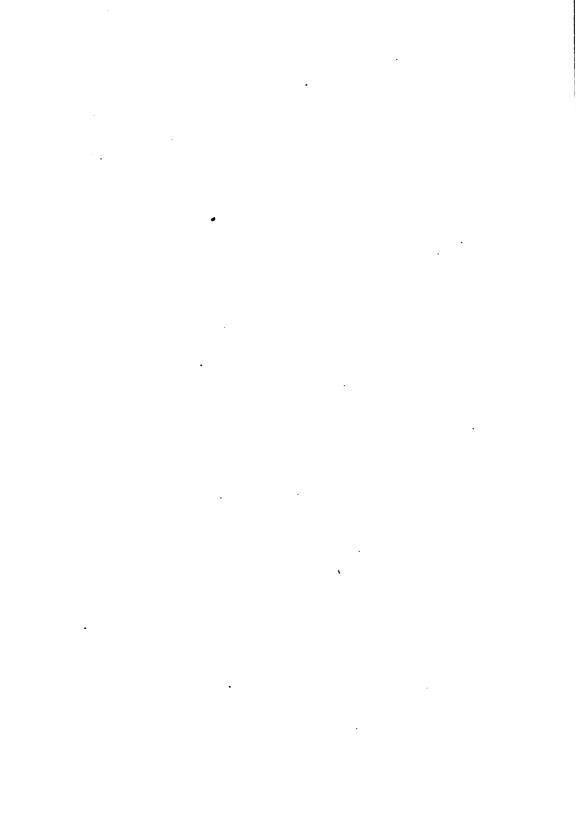
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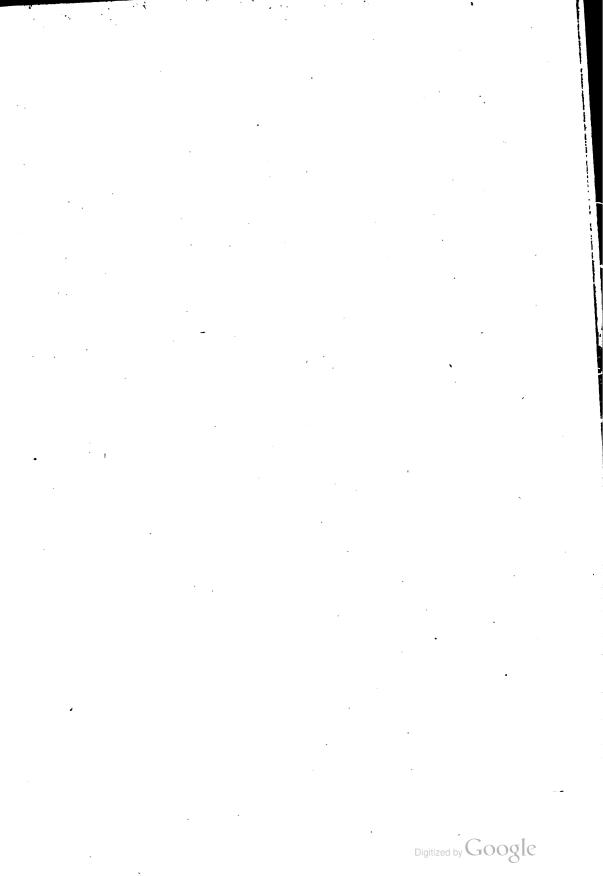


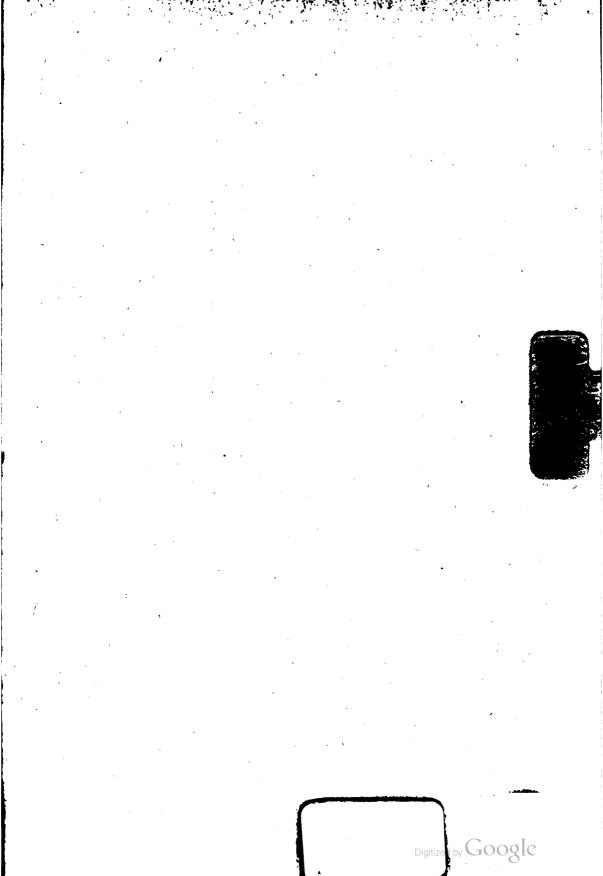
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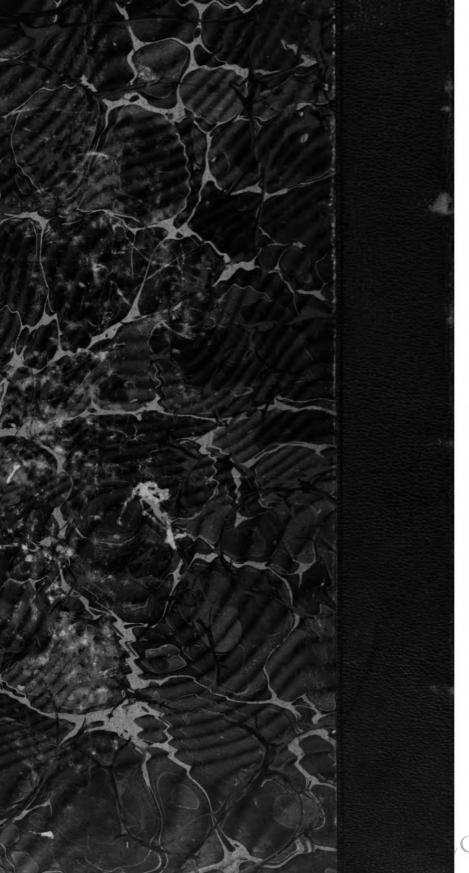
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